A THESIS

CRYSTAL AND MOLECULAR STRUCTURES OF SOME METAL NITRATO COMPLEXES

BY

DEREK WESLEY TAYLOR, B.Sc., M.Sc.

Submitted to the University of Glasgow for the degree of Doctor of Philosophy in the Faculty of Science

Chemistry Department June 1972

ProQuest LLC.
789 East Eisenhower Parkway
P.O. Box 1346
Ann Arbor, MI 48106 – 1346

ACKNOWLEDGEMENTS

The work described in this thesis was carried out in the Department of Chemistry at the University of Glasgow and the author would like to thank Professor J.M. Robertson and Professor G.A. Sim for providing the facilities to carry out this study and for their help and interest.

The author would like to express his sincere gratitude to his supervisor, Dr A.F. Cameron, for his helpful advice and encouragement, to Dr R.H. Nuttall who originally suggested studying metal-nitrate complexes, and to Dr K.P. Forrest who collaborated with me during the initial stages of the structure analysis of Bis[Dinitratobis(pyridine)-Copper(II)]pyridine.

Thanks are also due to other members of the department, especially Drs. J.G. Sime, D.M. Hawley, A.L. McDonald and Messrs. N.J. Hair and R.B. Dunlop for many helpful and stimulating discussions.

I am indepted to Professors D.W.J. Cruickshank and G. Ferguson, Drs. J.G. Sime, K.W. Muir, W.S. MacDonald, W. Oberhansli, D.R. McGregor and D.R. Pollard whose computer programs were used throughout this study.

The receipt of a Demonstratorship from the University of Glasgow is gratefully acknowledged.

SUMMARY

The first part of this thesis deals with some theoretical aspects of X-ray crystal-structure analysis with particular emphasis on those techniques employed in the present study. The previous structural work on metal nitrate complexes is then briefly reviewed and the results of X-ray structure determinations of ten metal-nitrato complexes with heterocyclic amines are described. The latter results are discussed in comparison with other known structures.

Many physical techniques have been used in attempts to rationalise the structures of series of metal nitrate complexes. In particular, spectroscopic evidence suggested that complexes of formula $A_2M(NO_3)_2$ [A = amine, M = Co(II), Ni(II), Cu(II) and Zn(II)] have structures similar to $Co(Me_3PO)_2(NO_3)_2$, i.e. six-coordinate with cis-bidentate nitrate groups. However, the structure analyses now reported of some bis-pyridine adducts of metal(II) nitrates have not revealed this stereochemistry.

The complex, $[Cu(py)_2(NO_3)_2]_2(py)$ (py = pyridine), is a centrosymmetric dimer with a bridging/chelating nitrate group of a type not previously found. In contrast, $Zn(py)_2(NO_3)_2$ has a monomeric, tetrahedral molecular structure with unidentate nitrate groups. It did not prove possible to isolate the anhydrous

bis-pyridine complexes of cobalt(II) and nickel(II) nitrates but one of the hydrates, $Ni(py)_2(NO_3)_2(H_2O)_2$, was examined. In this, the nickel has a fairly regular octahedral environment with oxygens of the nitrate groups involved in an extensive system of intermolecular hydrogen bonds with coordinated water molecules. The latter feature is expected to contribute to the stability of this complex.

There have been conflicting reports on the stereochemistries expected for the tris-pyridine complexes, $M(py)_3(NO_3)_2$ [M = Co(II), Ni(II), Cu(II), Zn(II) and Cd(II)]. These have been resolved by four separate X-ray structure determinations which all reveal distorted seven-coordinate molecular geometries. Three of the complexes [M = Co(II), Cu(II) and Zn(II)] may be considered grossly isomorphous although there are significant differences in the nitrato-coordination in each case. In the series examined, the asymmetry of the nitrate groups increases in the order Cd(II) $<$ Co(II) $<$ Zn(II) $\ll$ Cu(II). The anomalous position of $Cu(py)_3(NO_3)_2$ in this series is explicable in terms of a static Jahn-Teller effect.

The detailed mode of nitrato-coordination is particularly susceptible to changes in the metal environment. The latter part of the study has been to investigate the effect on the nitrate geometry of ligands having greater steric requirements than pyridine.

$Cu(\alpha\text{-pic})_2(NO_3)_2$ (α-pic = 2-methyl pyridine) was predicted to have a structure related to that of $Co(Me_3PO)_2(NO_3)_2$. However, the X-ray analysis has shown that the molecular geometry is very similar to $[\,Cu(py)_2(NO_3)_2\,]_2(py)$ although one of the axial sites of the copper is blocked by the presence of the α-methyl groups resulting in a monomeric species in this case. In a single-crystal e.s.r. and electronic spectral study of this complex by Professor B.J. Hathaway, a second crystalline form was discovered. Subsequent structural examination has revealed that the two forms exhibit an almost unique type of polymorphism with virtually identical molecular structures and unit cells, but different crystal packing.

The complex, $Cd(quin)_2(NO_3)_2$ (quin = quinoline) was found to have a seven-coordinate molecular structure similar to that of $Cd(py)_3(NO_3)_2$. Intermolecular hydrogen-bonding to oxygens of the nitrate groups is postulated although it is a <u>coordinated</u> nitrate-oxygen that is involved in contrast to the <u>terminal</u> oxygen utilised in $Ni(py)_2(NO_3)_2(H_2O)_2$. The nitrate groups are bidentate reflecting the size of the Cd(II) coordination shell in comparison with Ni(II).

CONTENTS

SECTION I

GENERAL INTRODUCTION

SECTION II

THE STRUCTURES OF SOME METAL-NITRATO COMPLEXES OF PYRIDINE

CHAPTER 1 BIS-PYRIDINE METAL-NITRATO COMPLEXES

CHAPTER 2 TRIS-PYRIDINE METAL-NITRATO COMPLEXES

SECTION III

THE STRUCTURES OF SOME METAL-NITRATO COMPLEXES OF AMINES WITH GREATER STERIC REQUIREMENTS THAN PYRIDINE

* Reprints also containing details of these structures are enclosed in the back of this thesis

SECTION I

GENERAL INTRODUCTION

CHAPTER 1

Some aspects of Crystal-Structure Analysis.

CHAPTER 2

The Structural Chemistry of Metal Nitrate Complexes.

CHAPTER 1

Some Aspects of Crystal-Structure Analysis

I.1.1. HISTORICAL

The early foundations of the science of crystallography were laid in the seventeenth century by Hooke, Huygens, Stensen (Sterno), Guglielmini and Delisle and other workers of this period, who were able to propose elementary theories of crystal structure based on a study of the external form of crystals. In 1784, Hauy discovered the fundamental law of rational indices and he considered that continued cleavage of a crystal would ultimately lead to a smallest possible unit, a 'molécule intégrante'. Bravais developed the idea of a crystal as a lattice structure and he showed geometrically that only fourteen distinct types of space lattice are possible. The 230 space groups were later derived by Federov and Schoenflies in 1890.

All of this early work proceeded without any means of examining crystals on an atomic scale. The means were provided by the discovery of X-rays by Röntgen (in 1895) and by von Laue's first X-ray diffraction experiment in 1912. The determination of the first crystal structures of some alkali-metal halides by Bragg immediately followed, showing that the exact locations of

atoms in crystals could be measured. At first, these determinations were limited to inorganic compounds in crystals of high symmetry but the development of new methods of analysis and the advent of high-speed electronic computers has led to the elucidation of many highly-complex crystal structures such as proteins [1].

I.1.2. THE DIFFRACTION OF X-RAYS BY CRYSTALS

A perfect crystal may be considered as a regular three-dimensional array of identical groups of atoms. This array is known as the crystal lattice, and knowledge of the dimensions of this lattice together with the wavelength of the radiation used completely determines the conditions for the diffraction of X-rays by a crystal.

The diffraction of X-rays by crystals was discovered by von Laue in 1912 [2], who was able to show that the phenomenon could be described in terms of diffraction from a three-dimensional grating (i.e. the crystal lattice). However, the equations derived by von Laue were not in a suitable mathematical form for the interpretation of experimental results and they were not fully utilised until W.L. Bragg noticed the similarity of diffraction to reflection and was able to derive a simple equation by treating X-ray diffraction as 'reflection' from planes in the lattice [3]. Bragg's

law, $2d \sin\theta = n\lambda$ (where θ = angle of incident and reflected rays from a crystal plane, d = interplanar spacing, λ = wavelength of radiation used and n = integer), places von Laue's treatment on a physical basis and has led to both the interpretation of X-ray spectra and the determination of crystal structures.

Bragg's law may be considered more conveniently in the form, $\sin\theta = \frac{n\lambda}{2}(1/d)$ . . . (1). Thus, $\sin\theta$ is inversely proportional to d, the interplanar spacing in the crystal lattice. This inverse proportionality may advantageously be replaced by a direct relationship by constructing a reciprocal lattice based on the quantity (1/d). The construction is achieved by allowing normals to all of the direct lattice planes (h,k,ℓ) to radiate from a lattice point defined as the origin. If each of these normals is terminated at a point $(1/d_{hk\ell})$ from this origin [$d_{hk\ell}$ = perpendicular distance between planes (h,k,ℓ)], the set of points produced is the reciprocal lattice. This construction has the merit that, instead of visualizing the direct lattice with a large number of planes of varying orientation, it is easier to think of the normals to the planes rather than the planes themselves.

I.1.3. DATA COLLECTION

The experimental side of a three-dimensional,

single-crystal, X-ray structural determination may be divided into two parts: (i) Geometry of diffraction which enables the elucidation of the size, shape and symmetry of the reciprocal and direct lattices; (ii) Assignment of an observed intensity to every point in the reciprocal lattice. In the structure determinations contained in Sections II and III below, the geometry of diffraction has been studied by photographic methods using both Weissenberg and Precession geometry. The intensity data has in some instances been obtained from visual estimation of photographic results and in other cases by counter measurement on a computer-controlled four-circle diffractometer. Details of these methods are available in many standard textbooks (e.g. [4, 5, 6, 7, 8, 9, 10]).

In the latter part of a diffraction experiment - the data collection - the quantity measured is the integrated intensity. A useful definition of this fundamental [5] is 'a measure of the total number of photons of the characteristic wavelength being used which are diffracted in the proper direction by a reciprocal lattice point passing from the outside to the inside of the sphere of reflection or vice versa.' (The sphere of reflection defines that region of space where Bragg's law is satisfied). Ultimately, the intensity data may be related to the distribution of diffracting electrons in the unit cell and the methods of calculating this

relationship are enumerated below.

I.1.4. FACTORS AFFECTING INTENSITIES

(a) Atomic Scattering Factor

The maximum scattering power (f) of an atom is the total scattering ability of all its electrons and is equal to the atomic number (Z). This atomic scattering factor, f, is formally defined [10] as the ratio of the amplitude of the radiation scattered by the atom to the amplitude of the radiation which an electron would scatter under the same conditions according to the classical theory, and is a function of $(\sin\theta/\lambda)$ (where θ is the scattering angle and λ the wavelength of the radiation) since the atom has a finite size. Scattering factors calculated by different methods for various atoms have a reliability dependent upon the electron density functions employed and are only accurately known for the hydrogen atom.

It is frequently sufficient to regard the relative scattering powers of different types of atoms as being the same independent of the radiation used. However, if the wavelength of the incident beam lies near an absorption edge in the scattering element, and the bound-electron scattering of the high-energy X-ray

photon is considered, anomalous scattering (or anomalous dispersion) occurs. This may be accounted for by representing the atomic scattering factor as a complex quantity

$$f = f_o + \Delta f' + i\,\Delta f'' \quad \ldots\ldots (2)$$

where $\Delta f'$ and $\Delta f''$ are the real and imaginary dispersion corrections. A study of anomalous dispersion can be employed to test for the centric nature of a structure and to distinguish enantiomorphic structures [11]. A further use is in direct structure analysis [12].

(b) Temperature Factor

Thermal motion causes the spreading out of the electron distribution of an atom which results in a decrease of the intensity of the scattered radiation. The value of the scattering factor corrected for thermal effects is given by

$$f = f_o \exp -B(\sin\theta/\lambda)^2 \quad \ldots\ldots\ldots (3)$$

$$\text{or } f = f_o \exp -8\pi^2 U(\sin\theta/\lambda)^2 \quad \ldots\ldots (4)$$

where f_o is the scattering factor for an atom at rest, the Debye factor, B, is related to U (the mean square displacement of an atom at right-angles to the reflecting plane) by $B = 8\pi^2 U$.

The above expressions for the corrected scattering factor are based on isotropic thermal vibrations. However, it may frequently be more appropriate

to consider the thermal motion as anisotropic and to describe the electron density by a triaxial ellipsoid. Non-equivalent atoms will have different ellipsoids and these will be differently orientated so that the correction term will be more complex. Cruickshank [13] has represented the scattering factor as

$$f = f_o \exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}\ell^2c^{*2} + 2U_{23}k\ell b^*c^* + 2U_{31}\ell ha^*c^* + 2U_{12}hka^*b^*)] \quad . . \quad (5)$$

For U_{ij}, i,j are with reference to the reciprocal axes a*, b* and c*.

(c) Some Geometric and Physical Factors

The most important quantity derived from the integrated intensities is the structure amplitude, $|F(hk\ell)|$. This quantity may be calculated from a knowledge of the positions of the atoms in the unit cell, and it is related to the empirically related intensities by $|F| \propto (I)^{1/2}$. This relationship depends upon a number of factors which are primarily geometric or physical and a consideration of these factors is facilitated by the adoption of the more informative equation

$$|F(hk\ell)| = \left[\frac{E(hk\ell)}{K.L(hk\ell).p(hk\ell)}\right]^{1/2} \quad . . . . . \quad (6)$$

where $L(hk\ell)$ = Lorentz factor, $p(hk\ell)$ = polarisation factor, and $E(hk\ell)$ = amount of energy diffracted in the

order (hkℓ) as an ideally imperfect crystal rotates uniformly about an axis normal to the X-ray beam. K is a constant which may be derived from a detailed knowledge of the radiation used, the geometry of the crystal, and some fundamental constants [4]. However, some quantity proportional to E(hkℓ) is normally measured and since the values thus obtained are on an arbitrary scale, the experimental constant K is usually disregarded.

The polarisation factor arises because the incident X-ray beam is not plane polarised. This factor, p(hkℓ) is given by:

$$p(hk\ell) = \frac{1}{2}\,(1 + \cos^2 2\theta) \quad \ldots\ldots (7)$$

and therefore is a simple function of 2θ and is independent of the method used for data collection.

L(hkℓ) is called the Lorentz factor and takes into account the fact that reciprocal lattice points pass through the sphere of reflection at different speeds. This factor varies with the method used for data collection. The form used for equi-inclination Weissenberg data is given by [14]

$$L(hk\ell) = \sin\theta \left\{1/\sin 2\theta\,(\sin^2\theta - \sin^2\mu)^{1/2}\right\} \quad \ldots (8)$$

where μ is the equi-inclination angle. For 4-circle diffractometer data or zero-level Weissenberg photographs, this expression reduces to

$$L(hk\ell) = 1/\sin 2\theta \quad \ldots\ldots\ldots (9)$$

Absorption, the most important of the physical factors, occurs because part of the X-ray beam is absorbed by the crystal and consequently its intensity is reduced. This can be expressed as:

$$I = I_0 \exp(-\mu t) \quad \ldots\ldots\ldots\ldots \quad (10)$$

where I_0 is the intensity of the incident beam, and I its intensity after it has passed through a thickness, t, of the crystal. The linear absorption coefficient, μ, is a function of the material of the crystal and the wavelength of X-rays employed. The absorption correction is particularly complicated for crystals that are not spherical or cylindrical. However, if the size of the crystal is very small and the linear absorption coefficient is not high then the error due to absorption becomes a very small quantity which is frequently ignored.

Another physical phenomenon affecting the intensities is called extinction, which results in attenuation of the incident beam when the crystal is in a diffracting position and thus the intensity of the diffracted beam is reduced. This effect depends primarily on the physical perfection of the crystal and corrections for it are either ignored or left until the later stages of a structure examination.

I.1.5. THE STRUCTURE FACTOR

In a series of atoms scattering X-radiation, the wave scattered from each atom is characterised by an amplitude f_1, f_2, f_3, . . . f_j (atomic scattering factors) and a phase constant. The net amplitude resulting from a combination of these waves is known as the structure amplitude, $|F|$. For a general plane the resultant is given by

$$F(hk\ell) = \sum_j f_j \exp\left\{2\pi i(hx_j + ky_j + \ell z_j)\right\} \quad . \quad . \quad . \quad (11)$$

the summation being carried out over all the atoms in the unit cell, and where x_j, y_j and z_j are the fractional coordinates of the atoms referred to the direct cell axes a, b, and c. Thus, the structure factor is a complex quantity and its constituents, the structure amplitude $|F|$ and phase constant α may be evaluated from

$$F(hk\ell) = (A_{hk\ell}^{\ 2} + B_{hk\ell}^{\ 2})^{1/2} \quad . \quad . \quad . \quad . \quad . \quad (12)$$

$$\text{or } \alpha(hk\ell) = \tan^{-1}(B_{hk\ell}/A_{hk\ell}) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

$$\text{where, } A_{hk\ell} = \sum_j f_j \cos 2\pi(hx_j + ky_j + \ell z_j) \quad . \quad . \quad . \quad . \quad . \quad (14)$$

$$\text{and } B_{hk\ell} = \sum_j f_j \sin 2\pi(hx_j + ky_j + \ell z_j) \quad . \quad . \quad . \quad . \quad . \quad (15)$$

These equations may be simplified by the presence of symmetry. For example, if the origin is chosen on a centre of inversion, $B_{hk\ell}$ becomes identically zero.

I.1.6. ELECTRON DENSITY

The structure of a crystal is periodic in three dimensions and therefore the electron density, ρ, at the point (xyz) can be expressed by a three-dimensional Fourier series. If each Fourier coefficient, C, is allocated three integral indices h', k' and ℓ', then

$$\rho(x,y,z) = \sum_{h'} \sum_{k'}^{+\infty} \sum_{\ell'} \left\{ C(h',k',\ell') \exp 2\pi i (h'x + k'y + \ell'z) \right\} \quad . \quad . \quad (16)$$

and it can be shown that

$$C(h',k',\ell') = \frac{1}{V} F(h,k,\ell) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

The structure factor is the Fourier transform of the electron density and can be expressed by

$$F(hk\ell) = \int_0^1 \int_0^1 \int_0^1 \left\{ V \rho(x,y,z) \exp -2\pi i (hx + ky + \ell z) \right\} dxdydz \quad . \quad . \quad . \quad (18)$$

where V is the volume of the direct cell and $V \rho(x,y,z)dxdydz$ is the amount of scattering matter in the volume element $Vdxdydz$.

From these equations it is apparent that if it were possible to determine the structure factors implicitly then it would be a relatively trivial matter to elucidate any crystal structure. However, it was shown above (I.1.4. and I.1.5.) that the structure factor

is a complex quantity and it is only possible to derive completely the structure amplitude, $|F|$, from the observed intensities. Thus, the fundamental problem in X-ray crystallography is to determine the phase angles, α, appropriate to these amplitudes and some of the methods of overcoming this difficulty are detailed below.

I.1.7. METHODS OF PHASE DETERMINATION

(a) Trial and Error

If it is possible to postulate an atomic arrangement for the compound under study which is consistent with the particular space group symmetry then, by calculating the corresponding structure amplitudes, $|F_c|$, and by comparing these with the moduli, $|F_o|$, derived from the observed intensities, it is possible to test the acceptability of this structure. Moreover, the proposed arrangement need not represent the complete structure. If a portion of the molecular framework is known, this may provide sufficient phases for the rest of the structure to be determined by successive structure-factor and electron-density calculations.

(b) The Patterson Function

Patterson [15] defined the function:

$$P(uvw) = V\int_0^1\int_0^1\int_0^1 \rho(xyz)\ \rho\left\{(x+u)(y+v)(z+w)\right\} dxdydz \quad . . \quad (19)$$

which is a convolution of the electron density with itself. If the expression given for the electron density (I.1.6) is substituted in this equation, this leads to

$$P(uvw) = \frac{1}{V} \sum_h \sum_k \sum_\ell |F(hk\ell)|^2 \exp\left\{2\pi i(h\underline{u}+k\underline{v}+\ell\underline{w})\right\} \quad . . . \quad (20)$$

A Patterson synthesis may therefore be regarded as a Fourier series summation with the phaseless quantities $|F(hk\ell)|^2$ as coefficients and the resulting map has peaks which correspond to the interatomic vectors.

For a molecule containing N atoms in a unit cell, there are N(N - 1) discrete interatomic vectors in the cell although resolution is generally poor because of the inherently greater spread of Patterson peaks in comparison with Fourier peaks. The latter problem may at least be partially solved by 'sharpening', i.e. applying an analytical function to the structure factors to consider the atoms as point atoms. However, for even a moderately complicated structure, it is still a formidable task to obtain the coordinates of all the atoms by inspection of the Patterson synthesis alone.

The symmetry of the Patterson function may not be exactly the same as that of the atomic distribution in the crystal, reflecting the loss of information involved in using the phaseless $|F|^2$ quantities. Comparison of the symmetries of the crystal space group and the Patterson

function shows that the lattice type remains the same, although the Patterson function is always centrosymmetric regardless of the space group from which it is derived. Moreover, all elements of symmetry involving translation are reduced to the corresponding non-translational ones.

Although some of the space group symmetry is lost in the Patterson, it is still detected in the form of specific concentrations of vector points. These concentrations, known as Harker lines and planes, arise because the vectors between corresponding atoms of molecules related by symmetry elements other than centres of inversion have one or two constant coordinates.

For a structure containing a heavy atom (or a few heavy atoms) whose scattering power dominates the intensity, the vectors between it and its symmetry-related equivalents will stand out strongly against the poorly resolved background of light atom peaks. The position of the heavy atom can therefore easily be obtained from the Patterson function and hence, the phases resulting from the heavy atom can be calculated. If this atom comprises the larger share of the structure factor, then a first approximation to the phases has been obtained and an electron-density distribution can be computed which may reveal the positions of some of the light atoms. Including these light atoms in the phasing model produces more accurate phases and thus, a closer representation to the true electron-density results. Through several cycles of such calculations, it is normally possible to completely

determine a complicated structure.

The so-called heavy-atom method is most successful when the sum of the squares of the atomic numbers of the heavy atoms is equal to that of the lighter atoms [5].

$$\text{i.e. } r = \sum Z^2_{\text{heavy}} / \sum Z^2_{\text{light}} \sim 1 \quad \ldots\ldots\ldots \quad (21)$$

When r = 1 and the structure is non-centrosymmetric, about 40 per cent of the reflections will have errors smaller than 20° in their phases and 80 per cent will have errors smaller than 60° [16]. For compounds where $r > 1$, the initial phases will be determined with greater accuracy. However, the accuracy of defining the positions of the lighter atoms is considerably reduced. If it is possible to obtain an isomorphous derivative containing light atoms only, then this structure may be determined using phases calculated for the heavy-atom compound. Subsequent refinement produces correspondingly more accurate coordinates for the light atoms. The isomorphous replacement method has found use in the study of structures of proteins.

Difficulties arise in structure elucidation if heavy atoms lie on or very close to special positions in the cell so that their symmetry is higher than that of whole molecules. This may lead to heavy-atom contribution to only a certain class of reflection while for the other reflections its contributions are out of phase and cancel. A Fourier map computed on the heavy atom alone therefore exhibits additional, false symmetry (pseudosymmetry) because

the systematic omission of a class of reflections imposes a higher symmetry on the entire structure. This problem is generally resolved by selecting a chemically reasonable part of the molecular framework from the pseudosymmetrically related peaks. Including this with the heavy-atom position in subsequent structure-factor and electron-density calculations is frequently sufficient to remove the false symmetry.

(c) Direct Methods

Direct methods rely upon examination of the intensity data alone and are gaining importance with the increased availability and efficiency of digital computers. The first of the methods were based on inequality relationships between structure factors depending only on the positivity of electron density [17]. However, when structures reach a certain size these inequalities are ineffective. In this situation the probability relationships deduced by Sayre are generally used which determine phases of one reflection in terms of other known phases. Normalised structure factors are generally used to evaluate the reliability of phases so determined. These are defined by

$$|E(hk\ell)|^2 = |F(hk\ell)|^2 / \varepsilon \sum_i^N f_i^2 \quad \ldots\ldots\ldots \quad (22)$$

where ε is an integer which is generally 1 but may assume other values for special sets of reflections in certain space groups. The distribution of $|E|$ values is dependent upon the presence or absence of a centre of inversion in

the space group and they therefore provide a statistical test for centric and acentric distributions of intensities.

The basis for the probability methods for the centrosymmetric case is the relationship [18]

$$F(hk\ell) = \phi(hk\ell) \sum_{h'} \sum_{k'} \sum_{\ell'} F(h'k'\ell').F(h-h',k-k',\ell-\ell') \quad \ldots . \quad (23)$$

where $\phi(hk\ell)$ is a simple scaling term. When $F(hk\ell)$ is large, Sayre has suggested that the series must tend strongly in one direction (+ or -) which is usually determined by the agreement in sign among products between large F's. Thus for three large reflections

$$S[F(hk\ell)].S[F(h'k'\ell')].S[F(h-h',k-k',\ell-\ell')] \approx +1 \quad \ldots \quad (24)$$

where S means the 'sign of'.

The probability of the above relationship being true, in general, is given by [19]

$$\text{Probability, } P = 1/2 + 1/2 \tanh \left\{ (\sigma_3/\sigma_2^{(3/2)}). |E(hk\ell).E(h'k'\ell').E(h-h',k-k',\ell-\ell')| \right\} \quad \ldots \quad (25)$$

where $\sigma_2 = \sum_i^N n_i^2$, $\sigma_3 = \sum_i^N n_i^3$; n_i is the fraction of the total scattering power represented by the ith atom.

The usual means of applying Sayre's equation to the determination of phases has been the symbolic addition method originally reported by Zachariasen [20].

In this method a small number of phases are arbitrarily assigned representing a choice of origin. These provide more phases in an inverted pyramid fashion. However, when this operation can proceed no further, other phases may be assigned symbols and the remainder determined in terms of these symbols, which can then be varied and the resulting set of phases checked mathematically. When a set of phases for the E's has been determined, a Fourier series can be summed using these normalised structure factors as coefficients and from this the structure, or a partial structure, may be deduced.

For non-centrosymmetric structures with generalised phases, the triple phase relationship[21]

$$\cos(\phi_h - \phi_{h'} - \phi_{h-h'}) \approx 1 \quad \ldots\ldots (26)$$

is frequently used. The reliability of this relationship may be measured by the variance of the probability distribution of the sum of the three phases. This can be expressed in terms of

$$K_{h,h'} = 2N^{-1/2} \left| E_h \cdot E_{h'} \cdot E_{h-h'} \right| \quad \ldots\ldots (27)$$

The problem with non-centric space groups is finding an initial set of phases. However, if there are several known pairs of phases giving a phase indication for an unknown reflection then its probable phase is given by the tangent formula[22]

$$\tan \phi_h = \frac{\sum_{h'} \left| E_{h'} \cdot E_{h-h'} \right| \sin(\phi_{h'} + \phi_{h-h'})}{\sum_{h'} \left| E_{h'} \cdot E_{h-h'} \right| \cos(\phi_{h'} + \phi_{h-h'})} \quad \ldots (28)$$

Thus, a large quantity of phases can be derived and the structure (or partial structure) may be determined by an E-map as indicated for the centric case above.

I.1.8. STRUCTURE REFINEMENT

When a model of the structure has been found or proposed it is necessary to have some criterion to judge its correctness. It has become a common usage to have as a criterion the comparison between observed and calculated structure factors in terms of the residual index, R, defined as

$$R = \frac{\sum \left| |F_o| - |F_c| \right|}{\sum |F_o|} \quad \ldots\ldots\ldots\ldots (29)$$

The purpose of refinement is to shift the derived atomic parameters so that they agree more closely with the real structure. The success of the refinement is reflected in decreasing values of R.

(a) Successive Electron-Density Distributions

In this method, the electron density is evaluated at appropriate points and the coordinates of the density maxima are determined and used as a basis for a new structure-factor calculation. Successive cycles are calculated until the changes in atomic parameters are insignificant.

The major drawback of the method is the series termination error which is due to only a finite number of Fourier terms in the calculation of the electron-density distribution. This means that the density maxima are not perfectly represented as points but instead as peaks of finite width surrounded by diffraction ripples. Thus, the problem is to estimate the centres of Fourier peaks and determine the best atomic coordinates. Several ways of dealing with this difficulty have been suggested [23] but these are not normally currently employed as the Fourier method is now mainly used only as an initial means of structure refinement.

(b) Least-Squares Methods

A crystal structure may be refined by the method of least-squares by minimising some function of the differences between the observed and calculated intensities with respect to the structural parameters. The function most commonly minimised is

$$M = \sum_{hk\ell} w(|F_o| - |F_c|)^2 = \sum_{hk\ell} w\Delta^2 \quad . \quad . \quad . \quad . \quad (30)$$

where the summation is over all structure amplitudes from independent observations and w is the weight of each term. If $\sigma^2(hk\ell)$ is the estimated variance of $|F_o(hk\ell)|$ due to random experimental errors, the value of w which gives the lowest standard deviation for the parameters refined is

$$w(hk\ell) = 1/\sigma^2(hk\ell) \quad \ldots\ldots\ldots\ldots \quad (31)$$

However, $\sigma^2(hk\ell)$ is normally not known and it is usual to use weights which reflect trends in the Δ's. A number of weighting schemes have been proposed and these may be tested by batching structure amplitudes according to $|F_o|$ sin θ/λ . The average value of $w\Delta^2$ should remain approximately constant however the data is batched. Moreover, at the end of the analysis the final value of $\sum(w|\Delta|^2)/(m - n)$ (m is the number of structure factors, n is the number of variables) should approach unity. In the present work, a weighting scheme of the form

$$w^{1/2} = \left\{[1 - \exp(-p_1(\sin\theta/\lambda)^2)] \,/\, [1 + p_2|F_o| + p_3|F_o|^2 + p_4|F_o|^3]\right\}^{1/2} \quad \ldots \quad (32)$$

was used, the p parameters being chosen to satisfy the above conditions.

In equation (30), for M to be a minimum

$$\frac{\partial M}{\partial p_j} = 0 \quad \text{where } j = 0, 1, 2, \ldots n \text{ parameters in the determination of } F_c.$$

<u>i.e.</u> $$\sum w \Delta \frac{\partial F_c}{\partial p_j} = 0 \quad \ldots\ldots\ldots\ldots \quad (33)$$

If the values of p_j are close to their true value and ε_i is a small change in the parameter p_i, it can be shown that

$$\sum_{i=1}^{n} \left[\sum_{hk\ell} w \frac{\partial F_c}{\partial p_i} \frac{\partial F_c}{\partial p_j} \right] \varepsilon_i = \sum_{hk\ell} w \Delta \frac{\partial F_c}{\partial p_j} \quad \ldots (34)$$

$$j = 1, 2, 3, 4 \ldots n$$

These n equations are called the normal equations of least-squares. For refinement, these simultaneous equations are solved to adjust the parameters so that the corrections become small in comparison with the estimated standard deviations. By these means, positional, thermal and scale parameters may be improved.

It is normally advantageous to express the normal equations in matrix form. The full normal matrix for n parameters has $\frac{1}{2} n(n + 1)$ unique elements which have in general to be kept in the main store of a computer simultaneously and require $\frac{1}{2} mn(n + 1)$ [m = number of observations] operations for their evaluation. Therefore, for large structures it is usual to omit the calculation of the off-diagonal elements as these are mostly small compared with those on the main diagonal and this radically reduces computer-store requirements. Convergence is reached more slowly when the block-diagonal approximation is used however, and care must be taken to select the correct number and types of parameters to be included in the blocks of normal-matrix to be computed to obtain maximum efficiency.

(c) Difference Synthesis

In a difference synthesis, a Fourier series is calculated on the basis of some model using as coefficients the ΔF's, i.e. the quantities $(|F_o| - |F_c|)$. If the proposed structure is close to the actual one, flat topography is expected in the difference map except for some undulatory characteristics caused by random error. Thus, difference Fourier calculations are used for structure solving, for structure refinement, and also to estimate the correctness of the final structure. The method is free from error resulting from the series termination effect and is frequently used to determine hydrogen positions from X-ray data.

I.1.9. ANALYSIS OF RESULTS

(a) Standard Deviations of Parameters

The standard deviations of the parameters (p_j) can be derived from the least-squares residual by the equation

$$\sigma(p_j)^2 = \frac{\sum w \Delta^2}{(m - n)\sum(\partial F_c / \partial p_j)} \quad \ldots\ldots (35)$$

or, in matrix notation

$$\sigma(p_j)^2 = (a^{-1})_{jj} \frac{\sum w \Delta^2}{(m - n)} \quad \ldots\ldots\ldots (36)$$

where $(a^{-1})_{jj}$ is the inverse matrix of a_{jj}, n is the number

of parameters and m is the number of independent observations. In the block-diagonal approximation, the inverse of the block-matrices is used in (36).

The co-variance of parameters p_i and p_j is given by

$$\text{cov}(p_i p_j) = (a^{-1})_{ij} \frac{\sum w \Delta^2}{(m - n)}$$

$$= \sigma(p_i).\sigma(p_j).r_{ij} \quad \ldots\ldots\ldots\ldots \quad (37)$$

where r_{ij} is the correlation coefficient between the parameters.

(b) Standard Deviation of Bond Lengths

The standard deviation of the bond length AB may be defined as

$$\sigma^2(\ell) = \sigma^2(A) + \sigma^2(B) \quad \ldots\ldots\ldots\ldots \quad (38)$$

where ℓ is the length AB, and $\sigma^2(A)$ and $\sigma^2(B)$ are the variance of A and B in the direction AB.

(c) Standard Deviations in Bond Angles

The standard deviation in the angle θ is given by [23]

$$\sigma^2(\theta) = \sigma^2(A)/AB^2 + \sigma^2(B)[(1/AB^2) - (2\cos\theta/AB.BC) + (1/BC^2)] + \sigma^2(C)/BC^2 \quad \ldots \quad (39)$$

where Θ is the angle ABC, $\sigma^2(A)$ and $\sigma^2(C)$ are the variance of A and C in plane ABC and perpendicular to AB and BC, while $\sigma^2(B)$ is the variance of B in the direction tangential to the circle ABC. The expression is valid for orthogonal axes, the general case being much more complex.

(d) Standard Deviations of Atoms from Least-Squares Planes

The estimated standard deviations of atoms from least-squares best planes is given by

$$\sigma^2(\text{plane}) = \sum_m d_m^2/(m - 3) \quad \ldots\ldots\ldots (40)$$

where d_m are the perpendicular distances of the m atoms from the plane.

CHAPTER 2

The Structural Chemistry of Metal Nitrate Complexes

I.2.1. INTRODUCTION

Although the anhydrous nitrates of several metals, in particular those of silver and the alkali metals, have been known for many years; the first anhydrous compounds containing the nitrate group with transition metals (Co, Cu, Mn and Ni) were isolated only in 1909 by Guntz and Martin [25]. However, it was not until 1954 when the first volatile nitrato-compounds of chromium and vanadium were prepared by Schmeisser and co-workers [26], that further support was added to that point of view which regarded the nitrate group as a reasonably strong complexing agent [27, 28]. Since that date many metals have been shown to form slightly volatile nitrates or highly volatile nitrato-compounds [29, 30] and it is now well established that in many of these cases the nitrate group is covalent, even when other strongly-donating ligands are present [31].

The first definitive structural reports of interest in nitrate chemistry were those of nitric acid [32], fluorine nitrate [33] and of some alkyl nitrates [33, 34] all of which contain unidentate nitrato-groups. Bidentate nitrato-groups were found in the structure of $UO_2[(EtO)_3PO]_2(NO_3)_2$ [35] and since this determination the majority of

nitrato complexes studied by diffraction techniques have contained this mode of bonding.

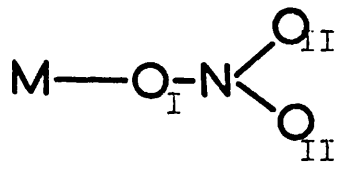
At this stage, it is worth considering the different modes of coordination that the nitrate group is expected to exhibit [36]. These are shown in Figure I.1. Apart from symmetric unidentate [I(i)] and terdentate bonding [IV] all of the other species have been experimentally identified. It is this large range of bonding possibilities and the fact that the chemical reactivity of nitrato-complexes varies widely with the multiplicity of the metal-nitrate bond [37], that has made structural investigations in this area of chemistry such a fruitful field.

There are a number of physical techniques, other than diffraction (X-ray, electron or neutron), which have been used in attempts to discover how many nitrate groups are coordinated in nitrate compounds and, if possible, the actual mode of bonding involved. The scope of some of these techniques will be briefly discussed in sections I.2.2 and I.2.3 and the resulting structural information is then considered.

FIGURE I.1

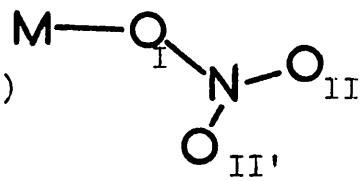
MODES OF COORDINATION OF THE NITRATE GROUP

(Notation after Addison et al [36])

I (i) 

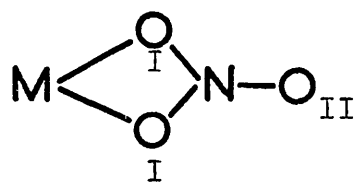
C_{2v}

SYMMETRICAL UNIDENTATE

(ii) 

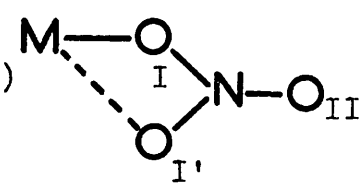
C_s

ASYMMETRICAL UNIDENTATE

II (i) 

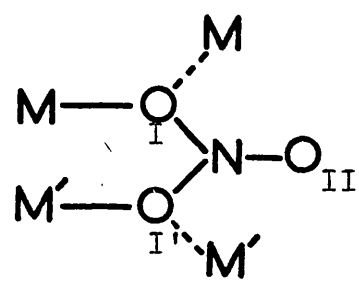
C_{2v}

SYMMETRICAL BIDENTATE

(ii) 

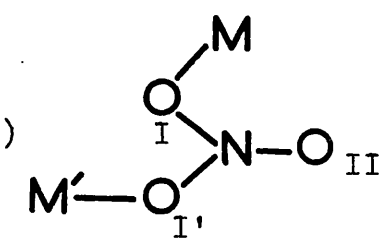
C_s

ASYMMETRICAL BIDENTATE

III (i) 

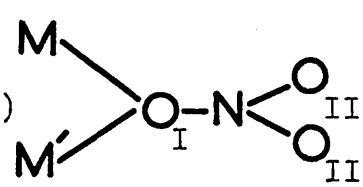
C_{2v}

BRIDGING (syn-syn or anti-anti)

(ii) 

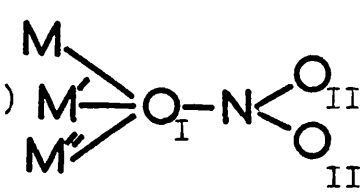
C_s

BRIDGING (syn-anti)

(iii) 

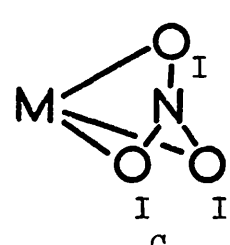
C_{2v}

BRIDGING

(iv) 

C_s

BRIDGING

IV 

C_{2v}

TERDENTATE

I.2.2. NUCLEAR MAGNETIC RESONANCE, ELECTRONIC SPECTROSCOPY AND VIBRATIONAL SPECTROSCOPY

Nuclear magnetic resonance has not been used to any great extent in nitrate chemistry mainly because of the low natural abundance of the isotopes ^{17}O and ^{15}N and the quadrupole broadening effect found for ^{14}N in an unsymmetrical electric field. Proton magnetic resonances have been used to obtain indirect information on the properties of the nitrate group although not on its mode of bonding (38, 39)

The electronic absorption spectrum of the free nitrate ion shows two strong bands assigned to $\pi^* \leftarrow n$ and $\pi^* \leftarrow \pi$ transitions. Coordination of the nitrate group causes the $\pi^* \leftarrow n$ band to shift to lower energy (40). However, this has not been used as a symptomatic test because of the common occurrence of charge-transfer transitions in the region of interest.

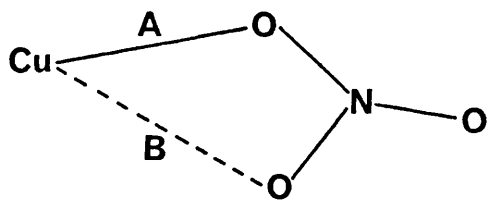
The major use of the electronic absorption spectra of transition-metal nitrato-complexes has been to predict stereochemistries and thus, indirectly, the mode of bonding of the nitrate groups. However, these predictions are not normally reliable because the low molecular symmetry that nitrato-complexes frequently exhibit does not allow unequivocal assignments to be made.

By far the most widely used technique for studying the nitrate group has been vibrational spectroscopy. The lowering of symmetry that occurs upon coordination [D_{3h}(free)$\longrightarrow$ C_{2v} or C_s(coordinated)] allows the free and coordinated nitrate group to be readily distinguished in the infrared and Raman spectrum. To determine the specific mode of coordination is more difficult and the techniques for achieving this have only involved two basic models: symmetrical bidentate and unsymmetrical unidentate. Although vibrational coupling frequently complicates assignments, the use of a combination of infrared and Raman spectroscopy often enables these modes of bonding to be distinguished. However, between these extremes exists a whole range of bonding possibilities. This is illustrated in Figure I.2 for some known Cu(II) nitrato-complexes. The wide range means that it is not generally possible to use vibrational spectroscopy as a routine method for investigating metal-nitrate coordination in the absence of other structural information.

The greatest current use for both electronic and vibrational spectroscopy in this area of chemistry has been to obtain bonding information for known structures. Perhaps in the future this assembled information will enable the structures of unknown compounds to be predicted more accurately using these techniques.

FIGURE I.2

Dimensions of asymmetric unidentate and bidentate nitrato-groups for some copper nitrate complexes



COMPLEX	REF.	A	B	(B-A)	Suggested Mode of Bonding
$Cu(Ph_2MeP)_3(NO_3)$	41	2.206	3.249	1.04	Unidentate (C_s)
$Cu(pyNO)_2(NO_3)_2$	42	1.97	2.80	0.83	Unidentate (C_s)
		1.97	2.75	0.78	
$Cu(NO_3)_2$(1,4-diazo-cycloheptane)$_2 0.5H_2O$	43	2.36	3.09	0.73	Unidentate (C_s)
$Cu(NO_3)_2(H_2O)_2 0.5H_2O$	44	1.992	2.653	0.66	Asym.Bidentate (C_s)
$Cu(NO_3)_2(MeCN)_2$	45	1.89	2.50	0.61	Asym.Bidentate (C_s)
$Cu(NO_3)_2$(pyrazine)	46	2.010	2.490	0.48	Asym.Bidentate (C_s)
$Cu(Ph_3P)_3(NO_3)$	47	2.22	2.22	0	Sym.Bidentate (C_{2v})
$Cu(NO_3)_2(g)$	48	2.00	2.00	0	Sym.Bidentate (C_{2v})

I.2.3. DIFFRACTION STUDIES

These techniques (X-ray, electron and neutron diffraction) fulfill two main functions in nitrate chemistry: i) to provide accurate dimensions for the nitrate group and determine implicitly the various modes of coordination; ii) to provide models for developing other physical methods of study. The latter point (ii) has been particularly important as the examination of electronic and vibrational spectra can be put on a more quantitative basis when dealing with known structures.

A large increase in structure determinations by diffraction methods in nitrate chemistry has occured in recent years. A review in 1967 [31] of nitrato complexes contained details of only twelve such structures whereas, in 1971, forty-seven nitrate structures were recorded [36]. In order to assess how representative these structures are it is useful to divide them into three categories:

I/ Anhydrous metal nitrates, or metals only coordinated by nitrate groups.

II/ Hydrated metal nitrates, or nitrates containing coordinated -OH.

III/ Nitrato complexes containing at least one coordinated ligand other than water.

The structures known at the present time are shown in Table I.I, where they are arranged according to the modes of nitrato-coordination found. The dividing line between

I.2.3. DIFFRACTION STUDIES

These techniques (X-ray, electron and neutron diffraction) fulfill two main functions in nitrate chemistry: i) to provide accurate dimensions for the nitrate group and determine implicitly the various modes of coordination; ii) to provide models for developing other physical methods of study. The latter point (ii) has been particularly important as the examination of electronic and vibrational spectra can be put on a more quantitative basis when dealing with known structures.

A large increase in structure determinations by diffraction methods in nitrate chemistry has occured in recent years. A review in 1967 [31] of nitrato complexes contained details of only twelve such structures whereas, in 1971, forty-seven nitrate structures were recorded [36]. In order to assess how representative these structures are it is useful to divide them into three categories:

I/ Anhydrous metal nitrates, or metals only coordinated by nitrate groups.

II/ Hydrated metal nitrates, or nitrates containing coordinated -OH.

III/ Nitrato complexes containing at least one coordinated ligand other than water.

The structures known at the present time are shown in Table I.I, where they are arranged according to the modes of nitrato-coordination found. The dividing line between

TABLE I.I

REPORTED METAL-NITRATO COMPLEXES

A. SYMMETRICAL BIDENTATE

I

$Ti(NO_3)_4$ [49]

$Co(NO_3)_3$ [50]

$Cu(NO_3)_2(g)$ [48]

$(Ph_4As)[Fe(NO_3)_4]$ [51]

$(Ph_4As)_2[Mn(NO_3)_4]$ [52]

$Mg_3[Ce(NO_3)_6]24H_2O$ [53]

$Mg[Th(NO_3)_6]8H_2O$ [54]

$Sn(NO_3)_4$ [55]

$(PPh_2Et)_2[Ce(NO_3)_5]$ [56]

$(NH_4)_2[Ce(NO_3)_6]$ [57]

$Rb[UO_2(NO_3)_3]$ [58]

$Cs[UO_2(NO_3)_3]$ [59]

II

$Th(NO_3)_4(H_2O)_32H_2O$ [60]

$[Th(NO_3)_3(H_2O)_3(OH)]2H_2O$ [61]

$UO_2(NO_3)_2(H_2O)_2$ [62]

$Pr(NO_3)_3(H_2O)_42H_2O$ [63]

III

$(Me_3PO)_2Co(NO_3)_2$ [64]

$(Ph_3P)_2Cu(NO_3)$ [47]

$[Ni(C_{10}H_{10}N_2)_2(NO_3)_2]NO_3$ [65]

$(bipy)_2La(NO_3)_2$ [66]

$(bipy)_2Tb(NO_3)_3$ [67]

$(Et_3PO_2)_2UO_2(NO_3)_2$ [35]

$(Et_3AsO)_2UO_2(NO_3)_2$ [68]

$Gd(NO_3)_2$[1,2-dipyridine-2-aldimino)ethane] [69]

$VO(NO_3)_3(CH_3CN)$ [70]

$Cd(py)_3(NO_3)_2$* [71]

$Ni(Me_4opda)(NO_3)_2$ [72]

* present work

TABLE I.I (cont)

B. ASYMMETRIC BIDENTATE

I $[Ph_4As]_2[Co(NO_3)_4]$ (73)

II $Cu(NO_3)_2(H_2O)_2 0.5H_2O$ (44)

$Cd(NO_3)_2(H_2O)_4$ (44a)

III $Cu(NO_3)_2(MeCN)_2$ (45)

$Cu(pyrazine)(NO_3)_2$ (46)

$Me_2Sn(NO_3)_2$ (74)

$[Cu(py)_2(NO_3)_2]_2py$ *(75, 76)

$Cu(\alpha\text{-pic})_2(NO_3)_2$ -Forms I & II *(77, 78, 79)

$M(py)_3(NO_3)_2$ (M = Co, Cu, Zn) *(80, 81)

$Cd(quin)_2(NO_3)_2(H_2O)$ *(82)

* present work

TABLE I.I (cont)

C. ASYMMETRIC UNIDENTATE

I $Li(NO_3)$[83]

$Na(NO_3)$[83]

$Cu(NO_3)_2.HgO.3H_2O$[85]

$K[Au(NO_3)_4]$[86]

II $Ni(NO_3)_2(H_2O)_4$[87]

$Zn(NO_3)_2(H_2O)_4$[88]

III $Cu(pyNO)_2(NO_3)_2$[42]

$Cu(NO_3)_2$(1,4-diazocycloheptane)$0.5H_2O$[43]

$Re(CO)_5(NO_3)_2$[89]

cis-$Pd(NO_3)_2(MeSO)_2$[90]

$VO(NO_3)_3(CH_3CN)$[91]

$Cu(PPhMe_2)_3(NO_3)$[41]

Cu(Me-picolyamine)$_2(NO_3)_2$[92]

$[Cu(NO_3)_2(bipy)_2](NO_3)H_2O$[93]

$MeSn(NO_3)_3H_2O$[94]

$Ni(py)_2(NO_3)_2(H_2O)_2$*[95]

$Zn(py)_2(NO_3)_2$*[96]

$[Ni(NO_3)(TRI)(H_2O)_2](NO_3)$[97]

Ag(2,2'dipy)$(NO_3)_2$[84]

* present work

TABLE I.I (cont)

D. BRIDGING

I	α-$Cu(NO_3)_2$	(98)
II	$Ni(NO_3)_2(H_2O)_2$	(99)
	$Cu(NO_3)_2(H_2O)_2 0.5H_2O$	(44)
	$Zn(NO_3)_2(H_2O)_2$	(100)
	$Cu_4(NO_3)_2(OH)_6$	(101)
III	$Cu(NO_3)_2(MeCN)_2$	(45)
	$Cu(NO_3)_2(MeNO_2)$	(102)
	$[Cu(py)_2(NO_3)_2]_2py$	*(75, 76)

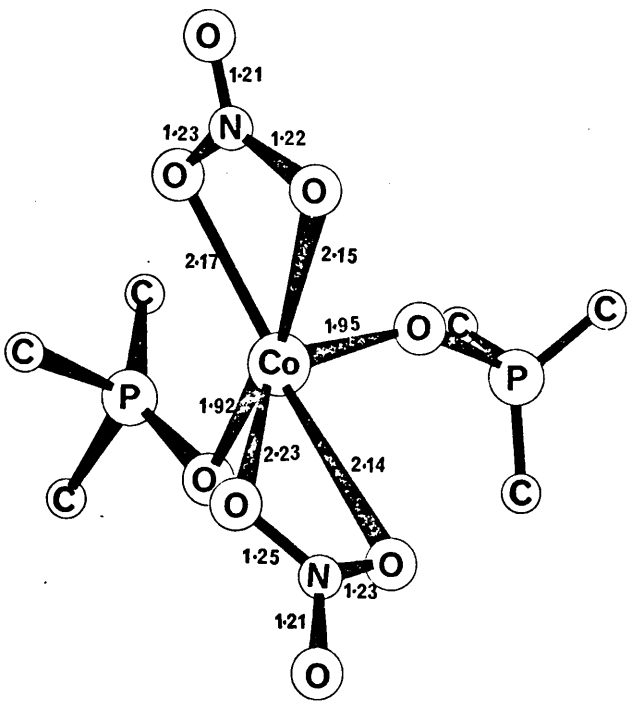
* present work

unidentate (C_s) and asymmetric bidentate (C_s) bonding is taken where the difference between the two closest metal-oxygen contacts exceeds 0.8Å (except for Zn(pyridine)$_2$-(NO_3)$_2$, see section II.1.4) as suggested by Addison et al [36], but this is a fairly arbitrary division and would be better made for individual complexes using, in addition, other physical techniques.

From the table, it is apparent that the vast majority of structural determinations carried out have been of compounds containing symmetrically bidentate nitrate groups. However, many of these compounds contain only coordinated nitrato-groups around the metal and the lack of steric repulsions from other ligands probably makes this mode of bonding most favourable. Another major class of compounds in this group are those of elements of high atomic number which are known to support coordination numbers greater than six. The main disadvantage of X-ray diffraction studies of compounds containing these elements is the high contribution to the scattering by the heavy metal atom which does not facilitate the determination of accurate dimensions for the nitrate group, and it is more satisfactory to limit our examination to complexes of first and second group transition metals. Complexes of these metals containing symmetrically bidentate nitrate groups and another ligand are not so well known and do not form a well-defined pattern. However, $(Me_3PO)_2Co(NO_3)_2$ has been used as a structural model for a great variety of subsequent spectroscopic studies [102a]

FIGURE I.3

MOLECULAR GEOMETRY OF $(Me_3PO)_2Co(NO_3)_2$ (64)


O
1·21
N
1·23
1·22
O
O
2·17
2·15
C
C
1·95
O
C
C
Co
P
P
1·92
2·23
2·14
O
O
C
C
1·25
N
O
1·23
1·21
O

of complexes of thy type $L_2M(NO_3)_2$ (L = unidentate ligand) and is worth considering in some detail.

The molecular geometry of $(Me_3PO)_2Co(NO_3)_2$ is shown in Figure I.3, and it is apparent that the nitrate groups are not strongly bonded to the cobalt (cf. $Co(NO_3)_3$ (50)). The overall stereochemistry of the complex may be thought of as distorted tetrahedral if the nitrate groups are considered to occupy single coordination sites. An alternative description is cis-distorted six-coordinate (C_{2v}), the approximate C_2 axis bisecting the two nitrate groups. No other example combining this type of geometry and nitrato-coordination has been found at present however, and it may well be that this complex was a fortuitous case where symmetrical bidentate bonding is allowed as a result of the relatively small steric requirements of the trimethylphosphine oxide ligands at bonding distances to the metal.

The other modes of nitrato-bonding are less well represented by reported structures but, in these examples, complexes of first-row transition metals (in particular of Cu(II)) predominate. For the hydrated metal nitrates a high degree of intermolecular association has been found. The tetra-aquo compounds achieve this through a network of hydrogen bonding whereas the diaquo-species associate through bridging nitrato groups. There are few known examples of bridging nitrate groups and, apart from the dihydrates of Ni and $Zn(NO_3)_2$, all other examples have been Cu(II) complexes.

Asymmetric bidentate and unidentate bonding can generally be rationalised by consideration either of steric effects or of hydrogen bonding to the nitrate groups. Asymmetric bonding is also frequently found in Cu(II) compounds resulting from the unsymmetrical electric field of the copper ion. However, all of the structures show such variety that, on present evidence, it is extremely difficult to reliably predict a priori the molecular geometries of nitrato complexes.

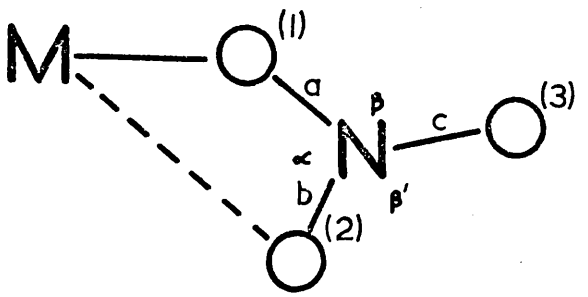
I.2.4. NITRATE DIMENSIONS

The nitrate ion in a regular environment is planar with all O-N-O angles equal to 120° and the N-O bonds of length 1.245 ± 0.01 Å [103]. After coordination to a metal, this planarity is generally retained and frequently includes the metal atom. However, the dimensions are distorted from the free ion values and the degree of this distortion may be related to the mode of bonding and to the strength of the metal-nitrate interaction.

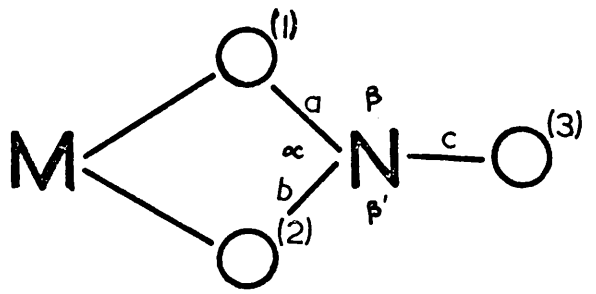
(i) Unidentate Bonding (C_s) and Asymmetric Bidentate Bonding (C_s) - I

The O-N-O interbond angle (β) opposite the strongest metal-oxygen interaction is increased from 120° while the other two angles (α, β') are generally less than 120°, with $\beta' > \alpha$ by an amount related to the strength of the M...O(2) interaction. Predictions [104, 105] from the magnitudes of the O-N-O angles in terms of the hybridisation of nitrogen σ-orbitals suggest N-O bond lengths in the order $b < c < a$, but changes in the π-bonding would suggest the order $c < b < a$. The latter order has been found to predominate and, although differences in length between c and b are not always statistically significant, they generally follow this trend. One recent exception to these predictions has been found in the structure of $(Ph_2MeP)_2Cu(NO_3)$ [41] where the

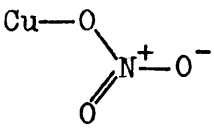
I



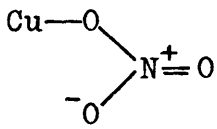
II



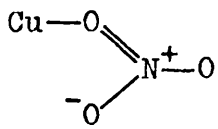
N-O bond lengths are in the order a < c < b. In this case the order has been explained in terms of a larger than normal contribution from a resonance form of type C in order to minimise the charge build up on the copper atom.



(A)



(B)



(C)

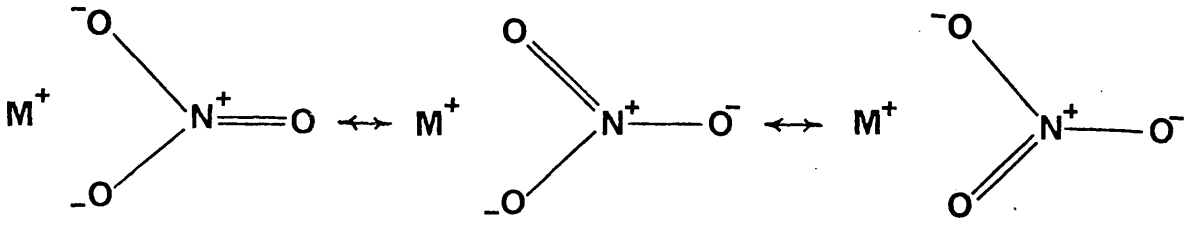
The M-O(1)-N angle (γ) has also been used as a guide to the mode of coordination of the nitrate group. It has been suggested [106], that a value of 110° for this angle is expected for normal (C_s) unidentate bonding although this value may be increased to ca. 120° by steric effects or by extensive hydrogen bonding. Values of γ less than 110° indicate an increasing M...O(2) interaction.

(ii) Symmetrical Bidentate Bonding (C_{2v}) - II

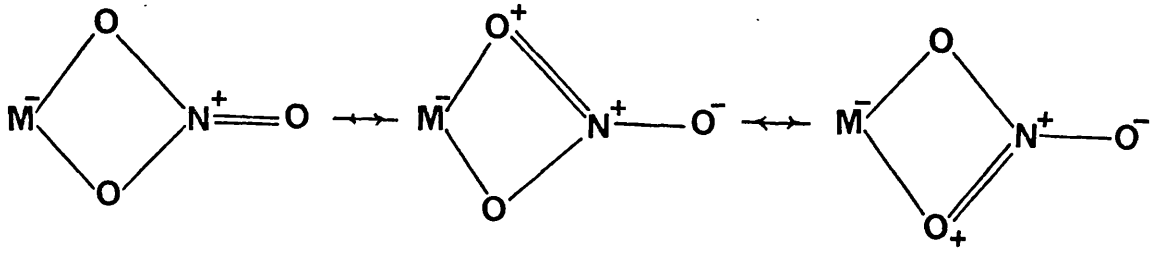
The O-N-O angle (α) between the coordinated oxygens is less than 120° while the other two angles (β, β') are correspondingly increased. The terminal N-O distance (c) becomes shorter while the N-O bonds involving the coordinated oxygens (a, a') become longer than the values found in the free ion. These changes can be explained using simple valence bond theory as this predicts that the σ N-O (coordinated) bonds have more nitrogen p-character than sp^2,

FIGURE I.4

IONIC INTERACTION



COVALENT INTERACTION



A B C

whilst the terminal oxygen atom has correspondingly less [107]. The effect of coordination on the π-bonding within the nitrate group is also expected to affect the N-O bond lengths in the sense observed, as the valence bond structure (A) should make the greatest contribution to the resonance structure of the molecule (Figure I.4). However, the strength of symmetric bidentate coordination covers a wide range and in compounds with fairly weak metal-nitrate interaction and it is difficult to appreciate the respective importance of covalence and polarisation phenomena.

For this mode of coordination, the M-O(1)-N angle ($\gamma \equiv$ M-O(2)-N) is expected to be ca. 95° although this varies within quite wide limits, e.g. for $Cu(NO_3)_2$ (g)[48] $\gamma = 85°$, and for $UO_2(NO_3)_2.6H_2O$ [62] $\gamma = 103°$.

(iii) Bridging (C_s and C_{2v}).

Not enough accurate data has been assembled to show reliable trends but, bond lengths and angles tend to vary in the same sense as indicated for unidentate and bidentate modes of bonding discussed above.

I.2.5. MOLECULAR GEOMETRY

A discussion of the molecular geometries expected of nitrato complexes is dominated by the fact that the nitrate group is a very compact ligand and has a short 'bite' of 2.1-2.2 Å. This means that the separation between the coordinated oxygens is much smaller than the sums of their van der Waals radii (2.80 Å [108]) and for complexes of ligands of this type, much higher coordination numbers are attainable than might otherwise have been expected.

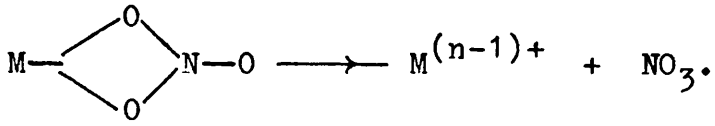
The size of the nitrate ion is similar to that of the chloride ion [31] and attempts to rationalise the stereochemistries of nitrato-complexes with similar complexes of simple ligands have been made. In this way, the tetranitrato-complexes of Ti(IV), Mn(II), Fe(III), Co(II) and Sn(IV) may be compared with the hexanitrato-complexes of Ce(III), Ce(IV) and Th(IV) by optimising the overall structures as tetrahedral and octahedral respectively and using radius-ratio criteria.

The concept of considering the bidentate (C_{2v}) nitrate group as occupying a single coordination site, with the direction of the ligand bisecting a line between the centres of the two coordinated oxygens, has been used by several workers [49, 64, 73, 109, 110]. This has the merit of enabling magnetic and spectroscopic properties to be explained on the basis of straightforward stereochemistries e.g. T_d or O_h etc. However, it has been pointed out [111-2]

that it is normally better to consider the bidentate nitrate group as occupying two coordination sites since the successful interpretation of physical properties for some Co(II) complexes using the simplified approach may merely have been fortuitous [113].

I.2.6. CHEMICAL REACTIVITY

Studies have shown that the more multiple the metal-nitrate bond becomes, the more reactive is the nitrate group [37]. Consideration of reactions with ethers have shown that ionic nitrates and asymmetric bidentate and unidentate nitrate-containing complexes are relatively inert. However, explosion with ether occurs with complexes such as $Ti(NO_3)_4$, $Sn(NO_3)_4$ and $Cu(NO_3)_2$ [114] which contain symmetrically bidentate nitrato-groups but this latter feature is not the sole criterion since other complexes containing this mode of bonding do not show the same order of chemical reactivity. It now appears that for the nitrate group to possess strong oxidising powers, it must be strongly bound to a metal atom which has a lower valency state readily available and moreover, that the species responsible for this reactivity is the NO_3. radical. A suggested mechanism [36] for the release of this radical is the homolytic fission of a metal-nitrate three-centre bond:



However, there is still a great deal of work to be done in understanding the chemistry of the nitrate group and a large part of this work must come from the elucidation of the basic structures.

SECTION II

THE STRUCTURES OF SOME METAL-NITRATO COMPLEXES OF PYRIDINE

CHAPTER 1

Bis-Pyridine Metal-Nitrato Complexes.

CHAPTER 2

Tris-Pyridine Metal-Nitrato Complexes.

INTRODUCTION

Complexes of pyridine with various metal salts are not only numerous, but also include a very wide range of possible stereochemistries. At present, pyridine complexes with metal halides have recieved the most systematic study and these commonly have the stereochemistries: tetrahedral, square-planar (cis and trans), octahedral (cis and trans), polymeric octahedral and distorted polymeric octahedral. In addition, certain individual complexes are known in which two separate isomeric forms can be isolated, e.g. α- and β-forms of $Co(py)_2Cl_2$ (115, 116) (py = pyridine). It is noticeable that all of these stereochemistries are based upon 4- or 6-coordinate metal ions. However, for metal-pyridine complexes containing polyanions, an even greater number of molecular geometries are possible with the increased range of available bonding possibilities. The latter class of compounds is not so well defined since the majority of postulated structures in this area have been based on magnetic and spectroscopic measurements and these have not been confirmed by X-ray diffraction studies.

Pyridine is an interesting non-aqueous solvent because it is a good base (pK_b = 8.81) with a low dielectric constant (ε = 12.3). Therefore, its transition metal complexes are of interest in the evaluation of

spectrochemical parameters and, in this field, a detailed knowledge of crystal structures is desirable [117, 118]. Crystal structures are also important for the accurate assignment of bands in the infrared and Raman spectra of pyridine complexes. The infrared spectra (4000-50 cm^{-1}) of free and coordinated pyridine has been the subject of much attention [119-23, 133-40], and the wide range of complexes available makes them useful prototypes in the study of more complicated systems.

Metal-pyridine complexes have also been studied because of their industrial importance as catalysts. For example, α,β and β,γ-unsaturated aldehydes and ketones capable of forming a conjugated dienol can be oxidised under mild reaction conditions in the presence of pyridine adducts of cupric acetate or nitrate [124, 125]. The advantage of the use of such complexes is that no side reactions occur in the oxidations but the detailed role played by the catalyst is not yet completely understood.

The structures of seven metal(II)-nitrato complexes with pyridine have been solved and are described in the following two chapters. Preceeding each discussion of these structures is a section describing some of the chemistry of other members of the series and indicating why the compounds studied were selected.

CHAPTER 1

Bis-Pyridine Metal-Nitrato Complexes

II.1.1 THE COPPER NITRATE-PYRIDINE SYSTEM

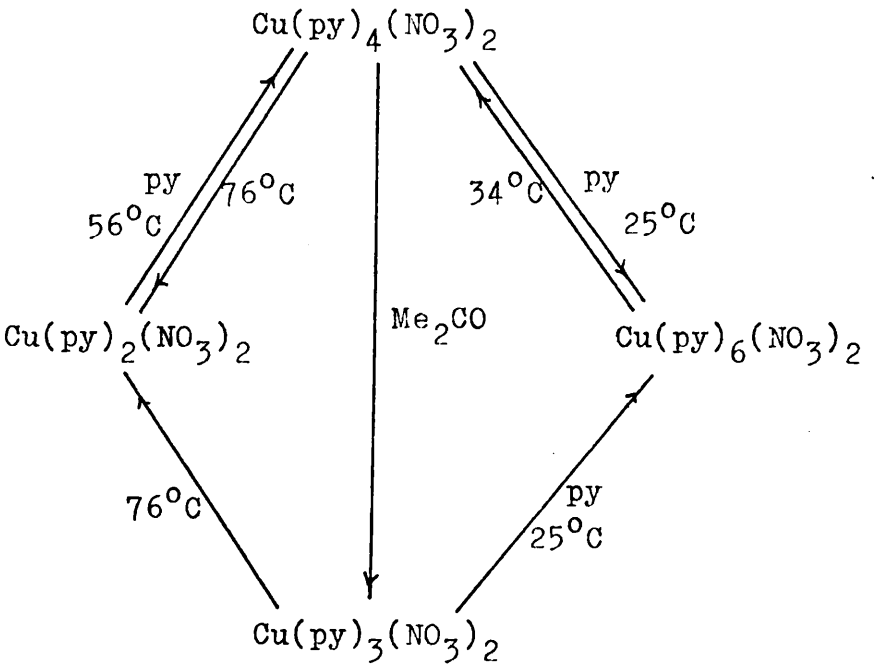
Pyridine forms a wide variety of complexes with anhydrous copper(II) nitrate. In the literature the following complexes have been reported: $Cu(py)_2(NO_3)_2$ (126-7), $Cu(py)_3(NO_3)_2$ (126, 127, 128, 130), $Cu(py)_4(NO_3)_2$ (126-7, 129, 131-2), $Cu(py)_5(NO_3)_2$ (131), $Cu(py)_6(NO_3)_2$ (126-7, 131), $Cu(py)_7(NO_3)_2$ (131). Biagetti et al (126), using thermogravimetric analysis, could only isolate the phases $Cu(py)_n(NO_3)_2$ (n = 2, 4 or 6) and they suggested that the existence of $Cu(py)_5(NO_3)_2$ and $Cu(py)_7(NO_3)_2$ was open to question as these complexes were only detected by vapour pressure measurements without analytical substantiation. The same workers could not find evidence for the existence of $Cu(py)_3(NO_3)_2$ as a separate phase but this complex has since been isolated in other studies (141, 145). An interrelationship diagram between these four phases, $Cu(py)_n(NO_3)_2$ (n = 2, 3, 4 or 6), is shown in Figure II.1 and their postulated structures are discussed below.

(a) $Cu(py)_4(NO_3)_2$

This complex has been prepared by two synthetic routes (126,132) and it has been suggested that these may lead to two separate structural forms as there are detailed

FIGURE II.1

Interrelationship diagram in the $Cu(NO_3)_2$-pyridine system



differences in their infrared spectra. Studies [126, 132] on both forms have shown that the nitrate and pyridine groups are all coordinated and a far infrared study [141] suggests that the simplest structure implied is octahedral, with four equatorial pyridine molecules and two long-bonded unidentate nitrato-groups. This type of structure has been found for many copper(II) complexes, e.g. $Cu(C_2N_2H_8)_2(NO_3)_2$ [142], $Cu(NH_3)_4(SCN)_2$ [143], $Cu(C_2N_2H_8)_2(BF_4)_2$ [144].

(b) $\underline{Cu(py)_6(NO_3)_2}$

The far infrared spectrum of this complex is very similar to that of the tetrakis-pyridine phase [141], and examination at the higher frequency end of the spectrum indicates the presence of both free and coordinated pyridine groups [126, 145]. The structure thus suggested is one with two pyridines of crystallisation and the nitrate groups still coordinated in a unidentate manner.

Since, from the available evidence these two complexes appear to offer no novel structural features, they have not yet been examined by single-crystal X-ray diffraction techniques.

(c) $\underline{Cu(py)_3(NO_3)_2}$

This complex is discussed in section II.2 below.

(d) $Cu(py)_2(NO_3)_2$

Biagetti et al [126] have suggested that $Cu(py)_2(NO_3)_2$ contains either bidentate or bridging nitrate groups on the basis of the splitting of the two highest nitrate frequencies in the infrared spectrum. The magnetic moment and electronic spectrum for this complex are significantly different from those for $Cu(py)_4(NO_3)_2$ and $Cu(py)_6(NO_3)_2$ but the reflectance spectrum is very similar to that recorded for $Cu(py\text{-}NO)_2(NO_3)_2$ [146] (py-NO = pyridine-N-oxide). An X-ray examination of the latter complex [42] has revealed a dimeric structure containing 'unidentate' nitrato-groups with oxygen-bridging through the organic ligands.

Far infrared studies of $Cu(py)_2(NO_3)_2$ [130,141 145, 147] have shown the presence of two bands attributable to copper-nitrato modes in a spectrum very similar to those recorded for other $CuL_2(NO_3)_2$ (L = unidentate ligand) complexes [147], and moreover, the large splitting observed for these modes in the bis-pyridine complex may well result from distortions present in the molecule. However, the ambiguities in these structural predictions justified a full examination of this complex by X-ray diffraction techniques.

II.1.2 CRYSTAL AND MOLECULAR STRUCTURE OF BIS[DINITRATOBIS(PYRIDINE)COPPER(II)]-PYRIDINE

II. 1. 2. CRYSTAL AND MOLECULAR STRUCTURE OF BIS[DINITRATOBIS(PYRIDINE)-COPPER(II)]PYRIDINE, $[Cu(py)_2(NO_3)_2]_2 \cdot py$

(a) Material Used in the Determination

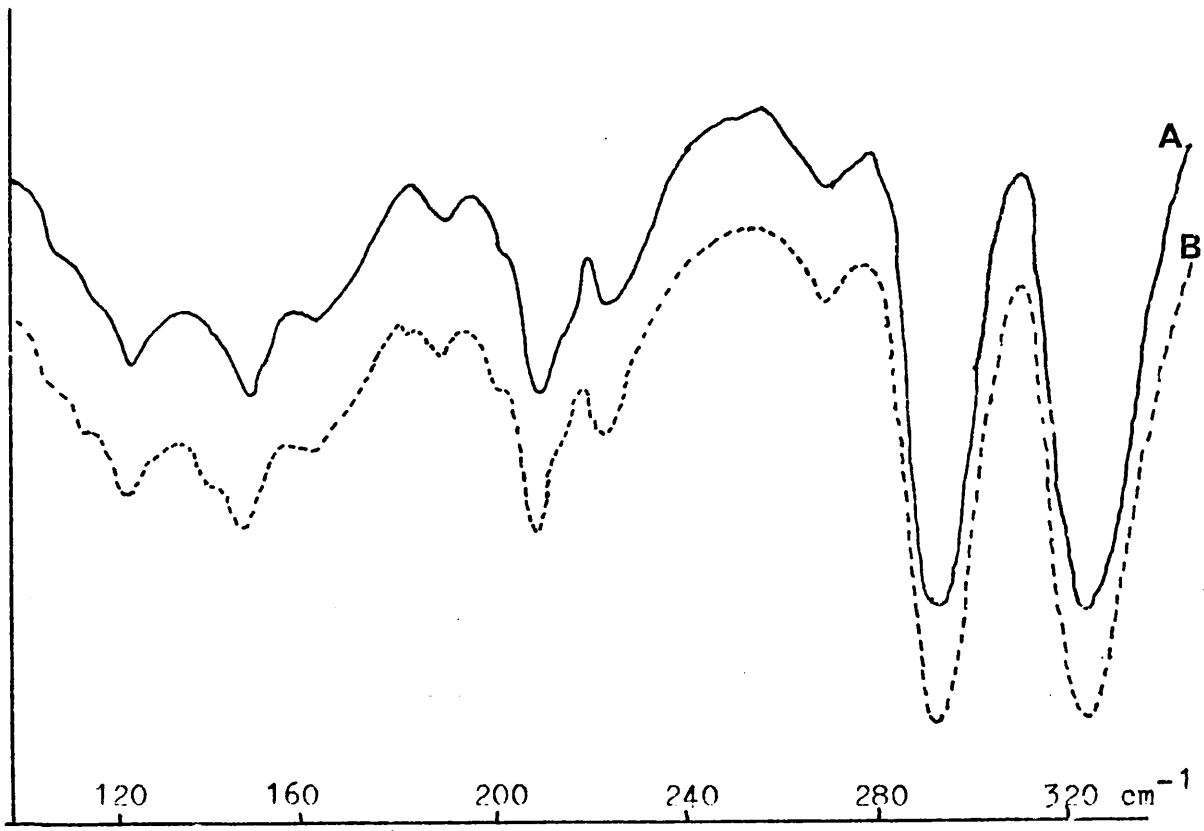
The complex was originally prepared[126] by the thermal decomposition of $Cu(py)_4(NO_3)_2$ (Figure II. 1), but this did not yield material suitable for a full X-ray diffraction study. An alternative preparative route was therefore found whereby a stoicheiometric amount of pyridine was added to a solution of anhydrous copper nitrate. The far infrared spectra of crystals obtained by this route and of the thermal decomposition product were compared and found to be identical (Figure II. 2) and it was adjudged that the nitrate groups were probably in a very similar environment in each case. The X-ray analysis was thus performed on one of the crystals prepared by the latter method.

(b) Experimental and Results

Full experimental details, atomic parameters, thermal parameters, and structure-factor tables are given in Appendix I.

Figures II. 3 and II. 4 show the atomic numbering scheme and the molecular packing respectively. Table II. 1 gives interatomic dimensions and Table II. II gives some least-squares best planes calculated through the molecule.

FAR INFRARED SPECTRA OF $Cu(Py)_2(NO_3)_2$



A Powder

B Crystals

Recorded at -196°C

FIGURE II.2

(c) Discussion

The analysis has revealed a centrosymmetric dimeric structure in which each copper atom is surrounded by seven other atoms in a distorted arrangement (Figure II. 3). The monomeric units are linked by interaction between the copper atom of one monomer and the copper-bonded oxygen [0(4)] of the other. This oxygen is therefore involved in unambiguous interaction with two copper atoms and is simultaneously bonded to the nitrate group of which it is part. This kind of bridging nitrate group is classified III(iii) in Figure I. 1 above and is the only example of this type of nitrato-bonding at present recorded. However, in the structure of the α-form of $Cu(NO_3)_2$ [98], in addition to the more normal bridging through two oxygen atoms of each nitrate group, the terminal oxygen is also involved in weaker interaction between two adjacent copper atoms. In the present structure, the Cu-0(4) and Cu'-0(4) distances are 2.042(6) and 2.542(8) Å, whilst in a α-$Cu(NO_3)_2$ the corresponding distances are 2.68(4) and 2.43(4) Å. Therefore, the important feature in the pyridine dimer is that it is a strongly-bound oxygen of the nitrate group that is involved in the bridging. Another example of bridging to a weakly-bound oxygen atom occurs in the seven-coordinate complex $Cd(CH_3CO_2)_2 \cdot 2H_2O$ [148] in which an asymmetrically bonded acetate group (Cd-0(1) 2.597(3), Cd-0(2) 2.294(4) Å) bridges to another cadmium atom (Cd' -0(1) 2.297(4) Å). Bridging/ chelating acetate groups are also found in the complexes $Ca[M(CH_3CO_2)_4]\,6H_2O$ [149] (M = Cu, Cd), and uranium (IV)

acetate [150].

Within the dimer, the inorganic sheet of the four nitrate groups and the two copper atoms is not greatly distorted from planarity, and the bonded pyridine molecules are not only orientated almost perpendicularly to this plane, but in addition are nearly parallel to each other. However, this is only a molecular feature as the space group symmetry does not allow the extension of these planes throughout the crystal. The trimeric nickel nitrite complex, $[Ni(\beta\text{-picoline})_2(NO_2)_2]_3$, also contains this feature of separate inorganic and organic sheets which has been suggested as an explanation for its marked stability [151]. This complex also shows two other interesting similarities with the Cu-pyridine dimer in that bridging of two nickel atoms by <u>one</u> oxygen from a nitrite group is present, and the unit cell was found to contain solvent molecules. In the dimer, the presence of free pyridine molecules on crystallographic centres of inversion raised speculation as to the validity of the original choice of space group, $P2_1/c$. The correctness of the space group was indicated by a trial refinement using the symmetry of space group Pc, and it was concluded that the solvated pyridines were statistically disordered. Thus, for refinement purposes, the solvated pyridine molecules were treated as benzene.

Although the inter-dimer separations are greater than van der Waals distances, the interaction of the free pyridine molecules with the dimers approach significant values C(11) . . . 0(2) 3.33, C(13) . . . 0(5) 3.60 Å. Since it is reasonable to suppose that the copper-nitrato coordination is not rigid, it

is difficult to decide the extent to which the internal geometry of the dimer may be affected by the close proximity of these molecules. However, a comparison of the molecular geometry of the dimer with other $Cu(NO_3)_2$ complexes [44, 46, 77-9] suggests that this feature is not of critical importance in defining the coordination of the nitrate groups.

In the dimeric structure, each copper atom is surrounded by seven immediately neighbouring atoms, although whether or not the copper can be considered seven-coordinate depends on the significance of the Cu-O(5) (2.906(7) Å) interaction. This distance is long compared with other copper-oxygen distances both in this and in other structures. However, the elongation of copper-oxygen bonds is well known [152] and the bonding significance of the Cu-O(5) interaction was examined by the calculation of overlap integrals using Slater orbitals [153, 154]. Although some gross oversimplifications are made, these calculations suggest that if copper-oxygen interaction is significant with a separation of 2.1 Å, then interaction will also be significant when the separation is 2.9 Å. Other work on tetragonal Cu(II) complexes supports this result [154].

An indirect method of testing the significance of the Cu-O(5) interaction is to examine whether the environment around the copper atom conforms to a stereochemistry normally expected for seven-coordinate systems. At present, the normally expected stereochemistries may be described as (1, 3, 3), (1, 4, 2), (1, 5, 1), (4, 0, 3) and may be theoretically predicted by consideration of the

equilibrium positions adopted by seven electron-pairs under an appropriate force law [155]. For the dimer, the arrangement around each copper atom approximates to that described as (1, 4, 2) which is a geometry known for the ions TaF_7^{2-}, NbF_7^{2-} and $NbOF_6^{2-}$. However, the lack of symmetry caused by the copper-oxygen long-bonds makes any such assignment inconclusive and an alternative description is a distorted pentagonal bipyramid (1, 5, 1) with the apical positions occupied by the pyridine nitrogens (Figure II. 5). This type of geometry is known for $Cr(O_2)_2(NH_3)_3$ [156], $Cr(O_2)_2(CN)_3^{3-}$ [157], $Cr(O_2)_2Ophen$ [158] and $Cr(O_2)_2H_2O(en).H_2O$ [159, 160] all of which show distortions in the equatorial plane although none so marked as in the present complex.

It has been suggested [49, 64, 73, 109, 110] that for complexes containing symmetrically bidentate nitrato-groups, the description of the molecular geometry is simplified by considering each nitrate group as occupying one coordination site with the direction of the ligands passing through the 'centre of gravity' between the coordinated oxygens. If it is reasonable to extend this argument to asymmetrically coordinated nitrate groups, then the geometry around each copper atom in the present complex could be regarded as distorted square-pyramidal. However, it is now thought that such approximations are, <u>in general</u>, unreasonable [36] and it is better to consider the interactions of the individual atoms.

A diagrammatic representation of the environment around each copper atom is shown in Figure II. 6. Superposition of

a grossly-distorted Jahn-Teller octahedral geometry on this system requires the Jahn-Teller short-bond positions to be occupied by the bonded pyridine groups and by an oxygen 0(1) and 0(4) of each nitrate group. The Cu-0'(4) dimerising bond occupies one of the long-bond axial positions, and although the site trans to this bond is vacant, the vector resultant of the Cu-0(5) and Cu-0(2) interactions would approximately complete the Jahn-Teller octahedron.

The preferred geometry for the Cu(II) ion with σ -bonding ligands is a distorted tetragonal octahedron and it is suggested [161] that bonding of groups in the axial positions cannot be ignored. For unidentate ligands the axial bond lengths tend towards ca. 0.6 Å longer than the equatorial distances, implying that the Cu(II) ion should be considered ellipsoidal rather than spherical. Therefore, the Cu-0'(4) dimerising bond (0.5 Å > in-plane Cu-0 distances) is of the correct order since the out of plane covalent radius of the Cu(II) ion has been estimated [162] to be ca. 1.90 Å. However, to justify the above picture of the coordination, it is also necessary to consider the evidence for the 'non-axial' bonding that has been postulated for 0(2) and 0(5).

Unfortunately, the fact that the molecules of $[Cu(py)_2(NO_3)_2]_2$ are not aligned in the crystal, makes the interpretation of single-crystal e.s.r. and electronic spectral measurements particularly difficult. It is therefore advantageous to obtain evidence for this type of bonding by analogy with other known Cu(II) systems.

Two complexes which have received extensive

study are $CaCu(CH_3CO_2)_4.6H_2O$ (I) [163, 164] and $Cu(HA)_4(ClO_4)_2$ (HA = 6-aminohexanoic acid) (II) [165, 166]. These contain both short (I 1.97 Å, II 1.93 Å) and long (I 2.79 Å, II 2.88 Å) Cu-O distances, and may be regarded as four or eight-coordinate, depending on the significance of the long interactions. Billing et al [167] have suggested that if the stereochemistry is considered to be square-planar in $CaCu(CH_3CO_2)_4.6H_2O$, an in-plane copper-oxygen bond length of ca. 1.91 Å and a value for the energy of the $d_{z^2} \rightarrow d_{xy}$ transition of ca. 19.0 kK would be predicted. The observed values for this complex were 1.97 Å and 12.5 kK respectively which are more reconcilable with a distorted octahedral stereochemistry and suggest some sort of coordination of the long-bonded oxygens. If, in the usual way, the short-bonded square-plane is defined as the xy-plane, then the other oxygens do not lie on the z-axis and some form of non-axial coordination was postulated. Although the precise nature of this coordination is not clear, the suggested model [167] for the two complexes above (I and II) may be adapted to describe the nitrato-bonding in the present dimer. The long-bonded oxygens of the nitrate group O(2) and O(5) are probably involved in sp^2 hybridisation, with the planes of the nitrate groups at right-angles to the xy-plane (Figures II.6 and II.7(a)). The orientation of one of these sp^2 lobes enables weak overlap with the d_{z^2} orbital of the copper (Figure II.7(b)). In the complex $CaCu(AcO)_4.6H_2O$, this type of description would explain the low energy of the $d_{z^2} \rightarrow d_{xy}$ transition [168] as the overlap is independent of the ground state of the Cu(II) ion.

It has further been suggested [167] that the p_z-orbital of long-bonded, non-axial oxygen atoms may be involved in weak π-bonding to the d_{xz} and d_{yz} orbitals of the copper although this is not so likely if there is a $d_{x^2-y^2}$ ground state.

It is interesting to compare the stereochemistry around the copper atom in the present dimeric complex with the geometries found in other known $Cu(NO_3)_2$ complexes in the light of this suggested bonding. It was mentioned above (II. 1. 1. (d)) that the reflectance spectra of $Cu(py)_2(NO_3)_2$ and $Cu(py\text{-}NO)_2(NO_3)_2$ are very similar [146] suggesting that the copper is in a closely-related environment in each case. The structure of the latter complex [42] reveals a centrosymmetric dimer, the monomeric units being linked through oxygen atoms of the C_5H_5NO groups. A diagrammatical representation of one of these monomeric units is shown in Figure II. 8 and the relationship with the pyridine complex (Figure II. 6) is obvious. Although the authors of the structure of $Cu(py\text{-}NO)_2(NO_3)_2$ did not consider that the long-bonded, non-axial oxygen atoms represented significant interaction, weak (sp^2-d_{z^2}) overlap may well be a feature to be considered.

In the structure of $Cu(NO_3)_2 \cdot 2 \cdot 5H_2O$ [44] the environment around the copper (Figure II. 9) again is very similar to that found in the pyridine and pyridine-N-oxide dimers. The long Cu-O distances (2.65, 2.68 Å) are of the same order as the Cu-O(2) distance (2.62 Å) in the present complex. This hydrated salt is polymeric with the monomeric units linked through one of the long-bonded oxygens of the nitrate group, i. e. an oxygen is bonded to a

nitrogen atom and to two separate copper atoms at Cu-O distances of 2.68 and 2.39 A. This weak bridging/chelating bonding is of the type found in α-$Cu(NO_3)_2$ [98] and $Cd(CH_3CO_2)_2 . 2H_2O$ [148].

An interesting comparison also exists between the structures of the present complex and of $Cu(\alpha\text{-pic})_2(NO_3)_2$ (α-pic = 2-Methylpyridine) [77, 78, 79] and this is discussed in Section III. 1.

In the complex $Cu(MeCN)_2(NO_3)_2$ [45], the same basic structure ensues (Figure II. 10) although, in this case only one of the non-axial oxygens can be expected to exhibit weak (sp^2-d_{z^2}) overlap. This is because the other nitrate group is arranged in an extended attitude with the terminal oxygen involved in strong bridging (Type III(ii), Figure I. 1) to another copper atom.

For all of the above complexes, the axial site on one side of the square-plane is either occupied or blocked. When this condition is absent, the long-bonded oxygens of the nitrate group may occupy 'trans' positions but the non-axial (sp^2-d_{z^2}) overlap is still a feature. An example of this kind of stereochemistry is the structure of $Cu(pyrazine)(NO_3)_2$ in which the long Cu-O distances are 2.490(5) Å [46].

Examination of the internal dimensions and stereochemistries of the nitrate groups in the present complex are of interest. Within the monomeric unit, the four atoms of each nitrate group are planar with the copper atom lying just off this plane (Table II. II). The dihedral angle between the nitrate planes is 15°. Moreover, it has been suggested that the high degree of polarisation to which coordinated nitrate groups are subjected

results in a distortion both of N-O bond lengths and of O-N-O angles [106]. Comparison of the N-O bond lengths with the terminal N(1)-O(3) (1.216(11) Å) and N(2)-O(6) (1.227(12) Å) bonds, shows that the oxygen atoms O(1) and O(4), which are involved in the strongest copper-oxygen interactions (Cu-O(1) 2.035(6), Cu-O(4) 2.042(6) Å), have sufficiently lengthened bonds to their nitrogen atoms (N(1)-O(1) 1.327(10), N(2)-O(4) 1.364(9) Å). In addition, O(2) is involved in an intermediate Cu-O interaction of 2.618(9) Å, and the N(1)-O(2) (1.261(11) Å) is just significantly longer than that for the terminal N-O bonds. However, O(5) which is involved in the (at best) weak Cu-O interaction of 2.906(7) Å, produces the N(2)-O(5) bond length of 1.228(10) Å which is experimentally identical to that of the terminal N-O bonds. There is thus a lengthening of N-O bonds in proportion to the degree of interaction between the copper and oxygen atoms as indicated by the copper-oxygen separations. Similar trends to these have been reported in the nitrate groups in $Cu(NO_3)_2 \cdot 2 \cdot 5H_2O$ [44], $Cu(py\text{-}NO)_2(NO_3)_2$ [42], $Cu(\alpha\text{-pic})_2(NO_3)_2$ [77, 78, 79] and $Cu(pyrazine)(NO_3)_2$ [46].

The corresponding internal valency angles of the two nitrate groups within the monomer are identical within experimental error, and while the mean values of 116.7, 118.6 and 124.7° are greatly different from the trigonal value of 120°, they suggest a slight systematic distortion of interbond angles arising from the coordination of the nitrate groups. The O-N-O angle opposite the strongest Cu-O interaction (O(2)-N(2)-O(3), O(5)-N(2)-O(6)) are increased from 120° as expected [106]. The Cu-O(4)-N(2)

(114.1(5)°) and the Cu-O(1)-N(1) (105.8(5)°) angles are significantly different, these values being consistent with the extent to which the nitrato groups may be considered bidentate on the basis of the Cu-O(2) and Cu-O(5) distances. Normally, a value in excess of 110° for this angle would suggest unidentate coordination [106], but the possibility of d_{z^2}-sp^2 non-axial overlap for Cu(II) does not allow such a clear-cut borderline.

The geometries and dimensions of the coordinated pyridine rings are in accord with literature values [169] for these groups and, apart from those intermolecular distances already mentioned, all other separations are greater than or equal to the sum of the relevant van der Waals radii.

TABLE II.1

$[Cu(py)_2(NO_3)_2]_2 \cdot py$

Interatomic distances (Å) and angles (°) with estimated standard deviations in parentheses

(a) Bonded distances

C(1)-C(2)	1.382(16)	O(1)-N(1)	1.327(10)
C(1)-N(3)	1.384(12)	O(1)-Cu(1)	2.035(6)
C(2)-C(3)	1.329(20)	O(2)-N(1)	1.261(11)
C(3)-C(4)	1.381(19)	O(2)-Cu(1)	2.618(8)
C(4)-C(5)	1.374(16)	O(3)-N(1)	1.216(11)
C(5)-N(3)	1.391(12)	O(4)-N(2)	1.364(9)
C(6)-C(7)	1.388(14)	O(4)-Cu(1)	2.042(6)
C(6)-N(4)	1.376(12)	O'(4)-Cu(1)	2.542(8)
C(7)-C(8)	1.413(16)	O(5)-N(2)	1.228(10)
C(8)-C(9)	1.406(16)	O(5)-Cu(1)	2.906(7)
C(9)-C(10)	1.385(15)	O(6)-N(2)	1.227(12)
C(10)-N(4)	1.398(11)	N(3)-Cu(1)	1.995(7)
C(11)-C(12)	1.284(36)	N(4)-Cu(1)	2.006(8)
C(12)-C(13)	1.372(39)		

TABLE II.1 (cont)

(b) Interbond angles

C(2)-C(1)-N(3)	121.4(9)	O(1)-N(1)-O(2)	118.1(7)
C(1)-C(2)-C(3)	121.3(11)	O(1)-Cu(1)-O(2)	55.3(3)
C(2)-C(3)-C(4)	119.4(12)	O(1)-Cu(1)-O(4)	168.0(2)
C(3)-C(4)-C(5)	117.2(11)	O(1)-Cu(1)-O(5)	141.9(2)
C(4)-C(5)-N(3)	122.2(9)	O(1)-Cu(1)-N(3)	90.2(3)
C(7)-C(6)-N(4)	121.2(9)	O(1)-Cu(1)-N(4)	88.9(3)
C(6)-C(7)-C(8)	118.7(10)	O(1)-Cu(1)-O'(4)	94.9(3)
C(7)-C(8)-C(9)	121.6(11)	O(2)-Cu(1)-O(4)	136.5(3)
C(8)-C(9)-C(10)	116.7(10)	O(2)-Cu(1)-O(5)	86.6(2)
C(9)-C(10)-N(4)	122.9(9)	O(2)-Cu(1)-N(3)	94.5(3)
C(11)-C(12)-C(13)	120.9(23)	O(2)-Cu(1)-N(4)	81.5(3)
N(1)-O(1)-Cu(1)	105.8(5)	O(2)-Cu(1)-O'(4)	161.6(3)
N(1)-O(2)-Cu(1)	80.7(5)	O(4)-Cu(1)-N(3)	90.4(4)
N(2)-O(4)-Cu(1)	114.0(5)	O(4)-Cu(1)-O(5)	50.0(2)
Cu(1)-O(4)-Cu'(1)	106.8(3)	O(4)-Cu(1)-N(4)	91.3(3)
N(2)-O(5)-Cu(1)	76.5(5)	O(4)-Cu(1)-O'(4)	73.2(3)
O(1)-N(1)-O(3)	117.1(8)	O(5)-Cu(1)-N(3)	92.3(2)
O(2)-N(1)-O(3)	124.5(9)	O(5)-Cu(1)-N(4)	85.9(2)
O(4)-N(2)-O(5)	119.0(7)	O(5)-Cu(1)-O'(4)	123.2(2)
O(4)-N(2)-O(6)	116.3(8)	N(3)-Cu(1)-N(4)	175.7(3)
O(5)-N(2)-O(6)	124.7(8)	N(3)-Cu(1)-O'(4)	89.1(3)
C(1)-N(3)-C(5)	118.3(8)	N(4)-Cu(1)-O'(4)	95.1(3)
C(6)-N(4)-C(10)	118.9(8)		

TABLE II.1 (cont)

(c) Intramolecular non-bonded distances

C(1). . .C(4)	2.77	C(11). . .C(13)	2.31
C(1). . .O'(4)	3.30	O(1). . .O(2)	2.22
C(2). . .C(5)	2.76	O(1). . .O(3)	2.17
C(3). . .N(3)	2.80	O(1). . .N(3)	2.83
C(5). . .O(4)	3.25	O(2). . .O(3)	2.19
C(5). . .Cu(1)	2.96	O(4). . .O'(4)	2.76
C(6). . .C(9)	2.82	O(4). . .O(5)	2.23
C(6). . .O(1)	3.22	O(4). . .O(6)	2.20
C(6). . .N(1)	3.83	O(4). . .N(3)	2.87
C(7). . .C(10)	2.77	O'(4). . .N(3)	3.21
C(7). . .O(1)	3.58	O(5). . .O(6)	2.18
C(7). . .O(3)	3.92	N(1). . .Cu(1)	2.72
C(8). . .O(2)	3.73	N(2). . .Cu(1)	2.88
C(8). . .N(4)	2.78	Cu(1). . .Cu'(1)	3.69

TABLE II.1 (cont)

(d) Intermolecular distances

O(1). . .C(7)^{I}	3.59	O(3). . .O(5)^{III}	3.45
O(2). . .C(11)^{II}	3.05	O(3). . .C(4)^{III}	3.47
O(3). . .C(5)^{III}	3.29	O(6). . .C(7)^{IV}	3.41
O(3). . .O(6)^{III}	3.31	O(6). . .C(8)^{IV}	3.46
O(3). . .N(2)^{III}	3.32	C(8). . .C(11)^{V}	3.63

Roman numerals as superscripts refer to the following equivalent positions with respect to the reference molecule at x, y, z:

I	-x, 1/2 + y, 1/2 - z
II	1 - x, 1 - y, -z
III	x, 1/2 - y, 1/2 + z
IV	x, -1/2 - y, -1/2 + z
V	x, 1/2 - y, 1/2 + z

TABLE II.II

$[Cu(py)_2(NO_3)_2]_2 \cdot py$

Least-squares best planes through the molecule. The equations are in the form $kX' + \ell Y' + mZ' = n$, where X', Y' and Z' are coordinates in Å. Distances of atoms from planes (Å) are given in square brackets.

	k	ℓ	m	n
Plane(1):				
C(1)-(5), N(3)	-0.4613	-0.6687	-0.5831	-1.8711
C(1) 0.015, C(2) 0.012, C(3) -0.007, C(4) 0.004, C(5) -0.006, N(3) 0.011, Cu(1) 0.058				
Plane(2):				
C(6)-(10), N(4)	-0.1983	-0.6553	-0.7289	-1.6154
C(6) -0.007, C(7) 0.009, C(8) -0.002, C(9) -0.007, C(10) 0.010, N(4) -0.002, Cu(1) -0.011				
Plane(3):				
O(1)-(3), N(1)	-0.4350	0.8022	-0.4089	0.2751
O(1) 0.026, O(2) 0.027, O(3) 0.041, N(1) -0.095, Cu(1) -0.181, O'(4) -0.148, Cu'(1) -0.370				
Plane(4):				
O(4)-(6), N(2)	-0.3589	0.6865	-0.6324	0.1380
O(4) 0.0003, O(5) 0.0003, O(6) 0.0003, N(2) -0.0009, Cu(1) -0.287, O'(4) -0.276, Cu'(1) 0.011				
Plane(5):				
O(1)-(6), N(1)-(2)	-0.4173	0.7461	-0.5188	-0.1536
O(1) 0.061, O(2) 0.195, O(3) -0.122, O(4) 0.135, O(5) 0.022, O(6) -0.170, N(1) -0.109, N(2) -0.013, Cu(1) 0.107				

TABLE II.II (cont)

	k	ℓ	m	n
Plane(6):				
O(1), O(4), N(3), N(4)	0.8916	0.4191	-0.1715	1.2809

O(1) -0.144, O(4) -0.140, N(3) 0.142, N(4) 0.142, Cu(1) 0.071, O(2) 2.149, O(5) 2.087, O'(4) -2.422

Dihedral angles (^{o}) between planes

Plane (1)-(2)	17	Plane (2)-(3)	82
Plane (1)-(3)	84	Plane (2)-(4)	85
Plane (1)-(4)	86	Plane (2)-(6)	71
Plane (1)-(6)	54	Plane (3)-(4)	15

FIGURE II.3

$[Cu(py)_2(NO_3)_2]_2py$

A view of the molecule along b showing the atomic numbering

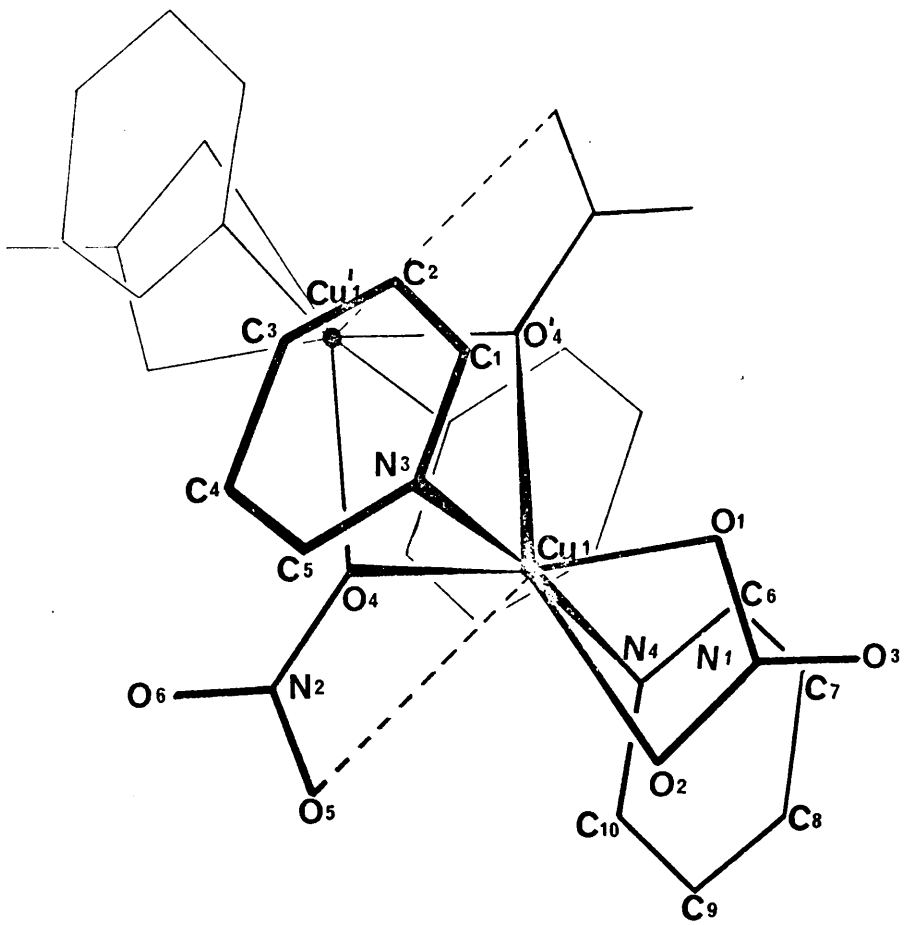
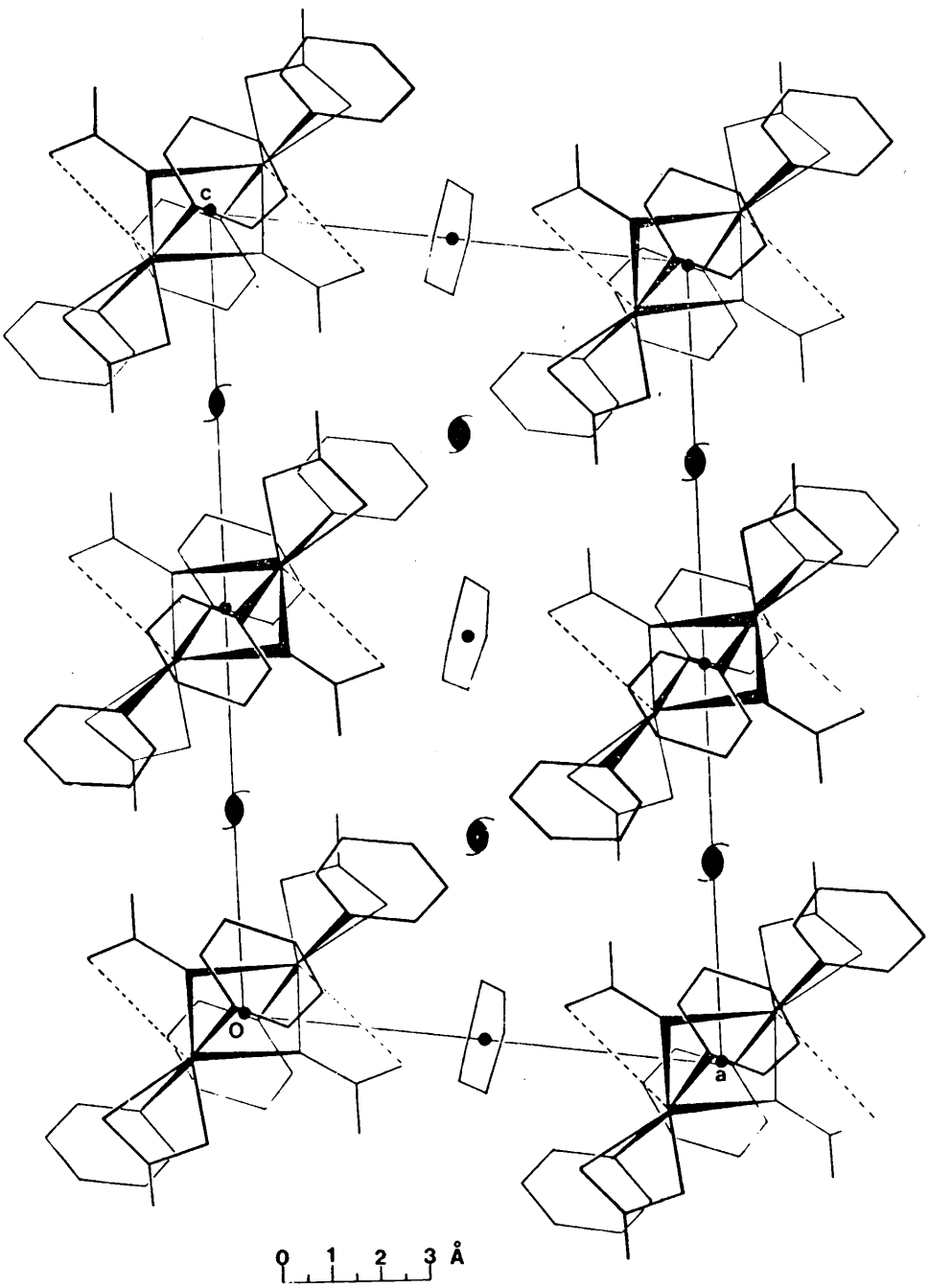

Cu'1
C2
C3
C1
O'4
N3
C4
C5
Cu1
O1
O4
C6
N4
N1
O3
O6
N2
C7
O2
O5
C10
C8
C9

FIGURE II.4

$[Cu(py)_2(NO_3)_2]_2py$

The molecular packing viewed along the b axis


c
O
a
0 1 2 3 Å

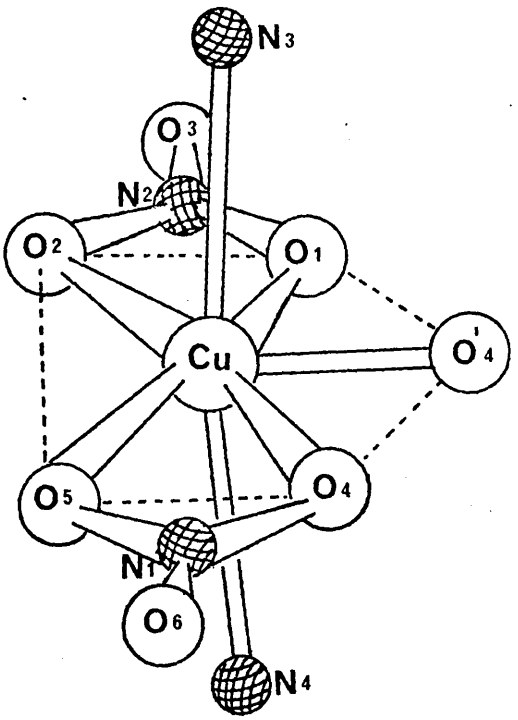


FIGURE II.5

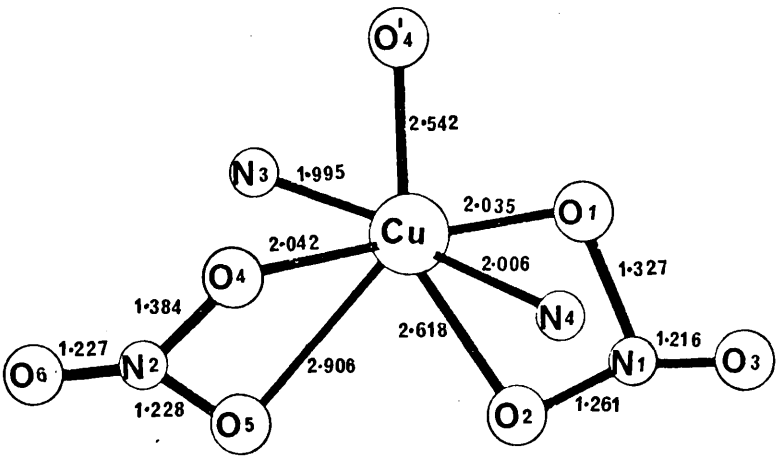
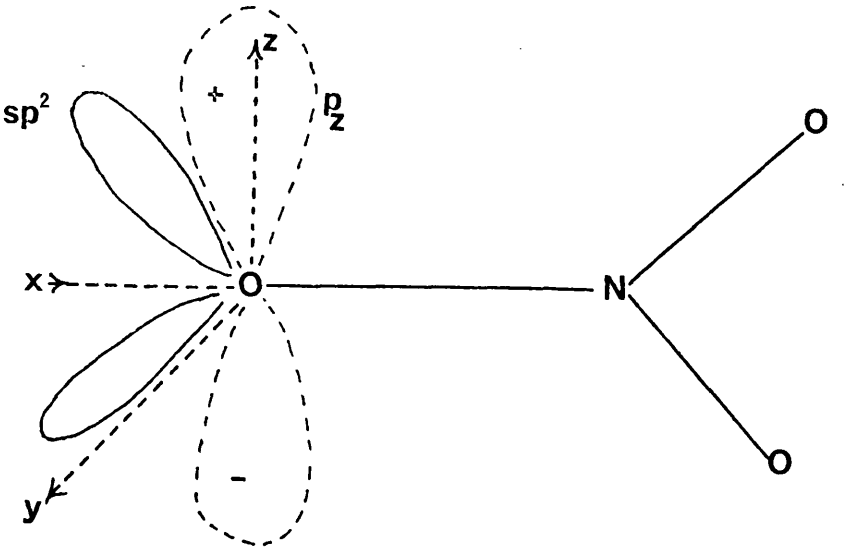
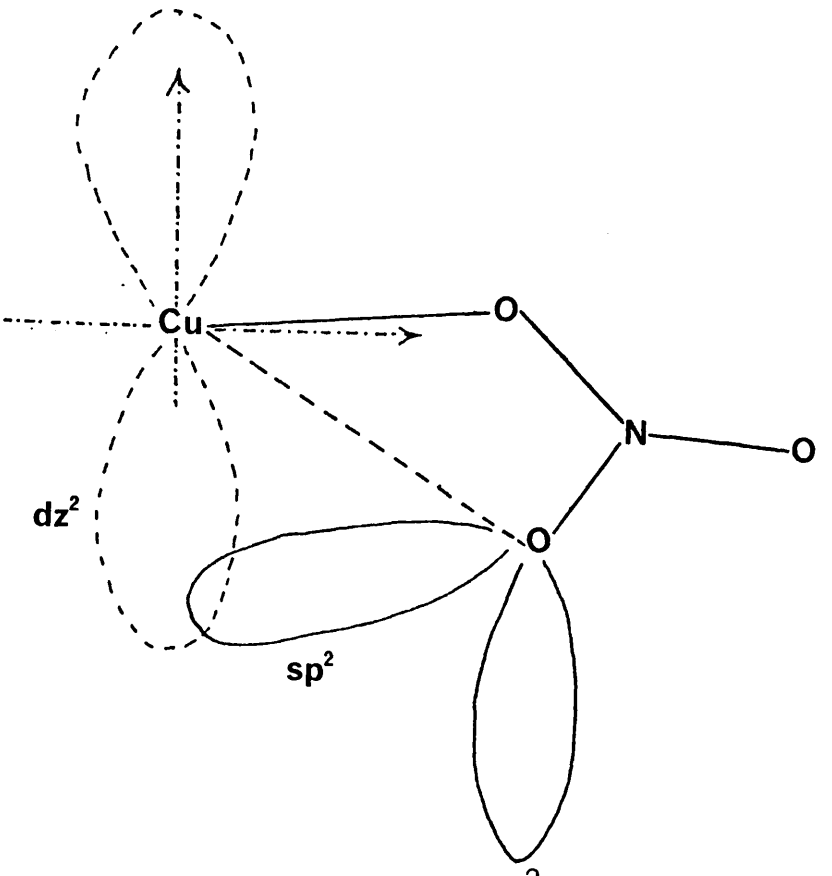


FIGURE II.6

A diagrammatic representation of the environment around each copper atom



(a) Hybridisation of long-bonded oxygens



(b) Overlap of long-bonded oxygen sp^2 hybridised orbital and the copper d_{z2} orbital

FIGURE II.7

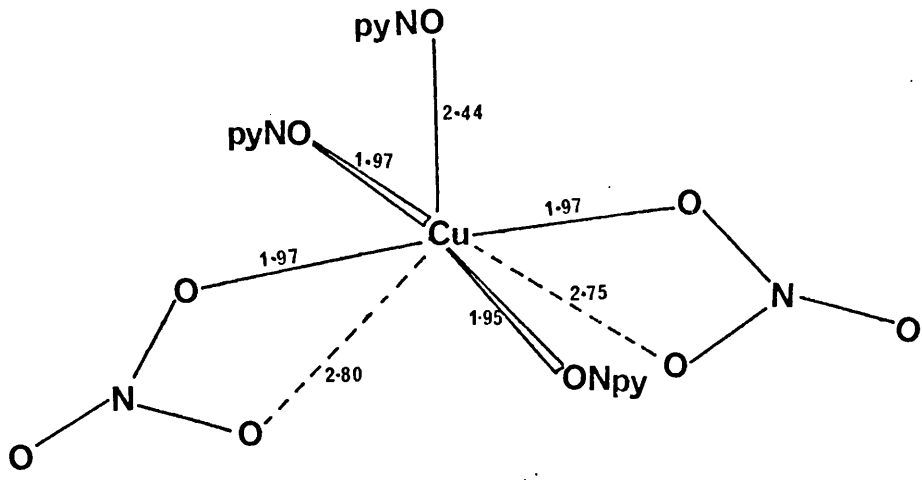


FIGURE II.8

Copper atom environment in $Cu(py\text{-}NO)_2(NO_3)_2$ (42)

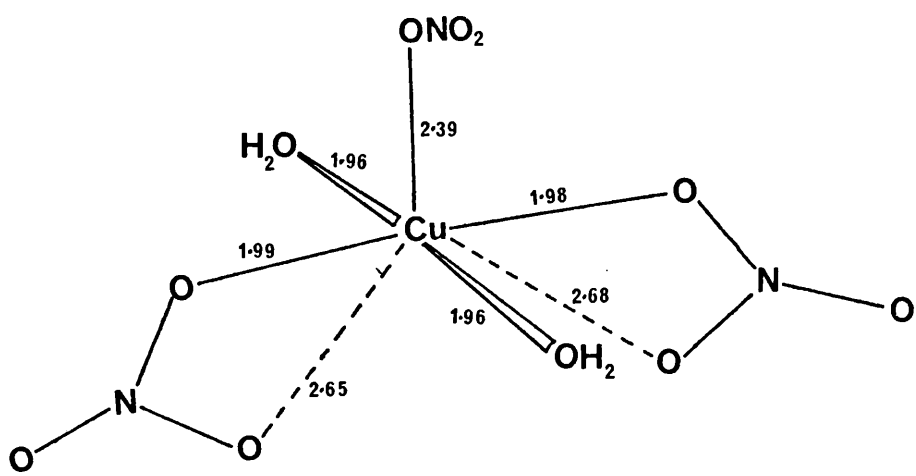


FIGURE II.9

Copper atom environment in $Cu(NO_3)_2 \cdot 2{\cdot}5H_2O$ (44)

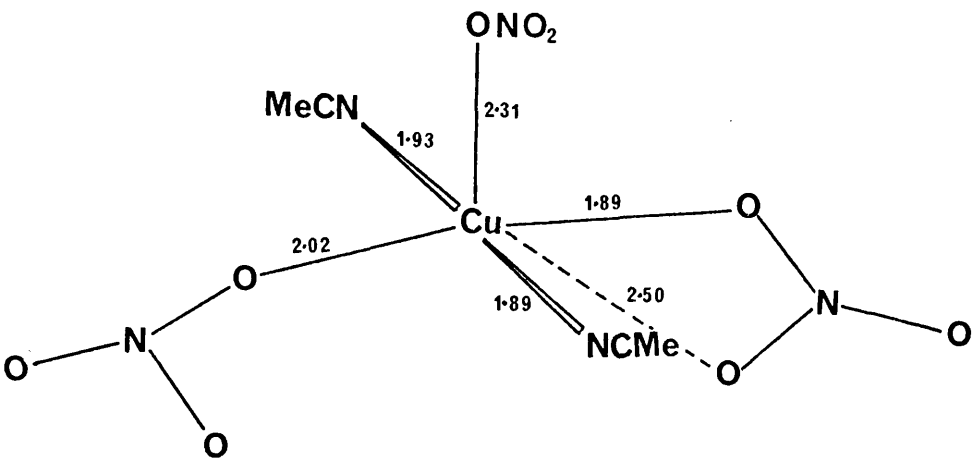


FIGURE II.10

Copper atom environment in $Cu(MeCN)_2(NO_3)_2$ (45)

II. 1. 3. THE ZINC NITRATE-PYRIDINE SYSTEM

Only three adducts of pyridine with anhydrous zinc nitrate have definately been identified: $Zn(py)_2(NO_3)_2$ [170, 141, 145, 147], $Zn(py)_3(NO_3)_2$ [130, 141, 145, 170] and $Zn(py)_6(NO_3)_2$ [141, 145, 170]. Compounds intermediate in formula between $Zn(py)_2(NO_3)_2$ and $Zn(py)_3(NO_3)_2$ have been reported [141, 145], but examination of their far infrared spectra shows composite features suggesting that they are mixtures rather than separate phases. An interrelation diagram between the separate complexes is given in Figure II. 11 and their suggested structures are discussed below.

(a) $Zn(py)_3(NO_3)_2$

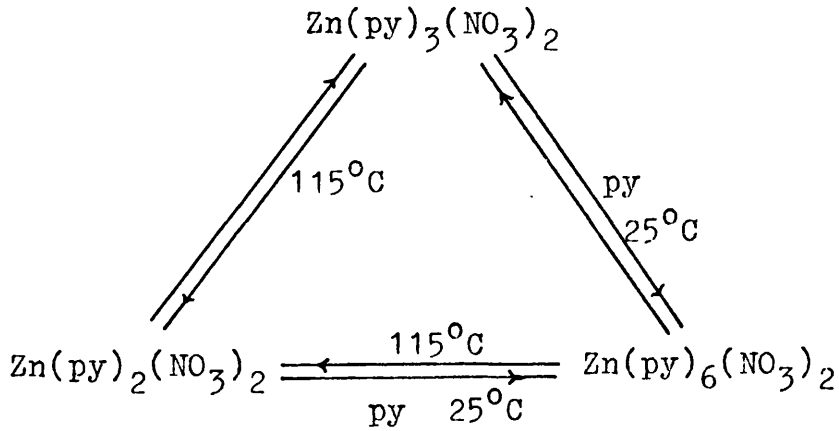
This complex is discussed with the other tris-pyridine complexes in section II. 2 below.

(b) $Zn(py)_6(NO_3)_2$

$Zn(py)_6(NO_3)_2$ was prepared by Ouellette and Haendler [170] by absorption of pyridine on the tris-pyridine complex. The reaction is readily reversible suggesting that the pyridine is absorbed into the lattice rather than entering the coordination shell of the zinc. Bands assignable to free pyridine frequencies in the infrared spectrum [145, 170] of the complex support this interpretation and further evidence for formulation as

FIGURE II.11

Interrelationship diagram for the $Zn(NO_3)_2$-pyridine system



$[Zn(py)_3(NO_3)_2]$ 3py is the almost identical far infrared spectra of the hexakis and tris-pyridine complexes.

(c) $\underline{Zn(py)_2(NO_3)_2}$

Haendler [170] has suggested from infrared measurements that this complex has tetrahedral geometry although other stereochemistries are certainly possible. However, he does not unambiguously differentiate between a true tetrahedral geometry with unidentate nitrate groups, and a quasi-tetrahedral structure such as that found for $(Me_3PO)_2Co(NO_3)_2$ [64] (Figure I. 3) in which the nitrate groups are symmetrically bidentate. Moreover, there are further possibilities of either a structure intermediate between these two extremes in which the nitrate groups are asymmetrically bidentate or a more complicated structure with bridging nitrate groups. An X-ray examination was carried out to resolve these ambiguities and to compare the structure with other bis-ligand complexes of metal(II) nitrates.

II.1.4 CRYSTAL AND MOLECULAR STRUCTURE OF DINITRATOBIS(PYRIDINE)-ZINC(II)

II. 1. 4. CRYSTAL AND MOLECULAR STRUCTURE OF DINITRATOBIS(PYRIDINE)-ZINC(II), $Zn(py)_2(NO_3)_2$

(a) Material Used in the Determination

Ouellette and Haendler [170] prepared $Zn(py)_2(NO_3)_2$ by the thermal decomposition of the tris-pyridine complex. As this material was not suitable for a full X-ray determination, the alternative route of adding a stoicheiometric amount of pyridine to an anhydrous solution of $Zn(NO_3)_2$ was used to obtain crystals. The far infrared spectra of the powder and the crystals were almost identical (Figure II. 12) and one of these crystals was used for the present study.

(b) Experimental and Results

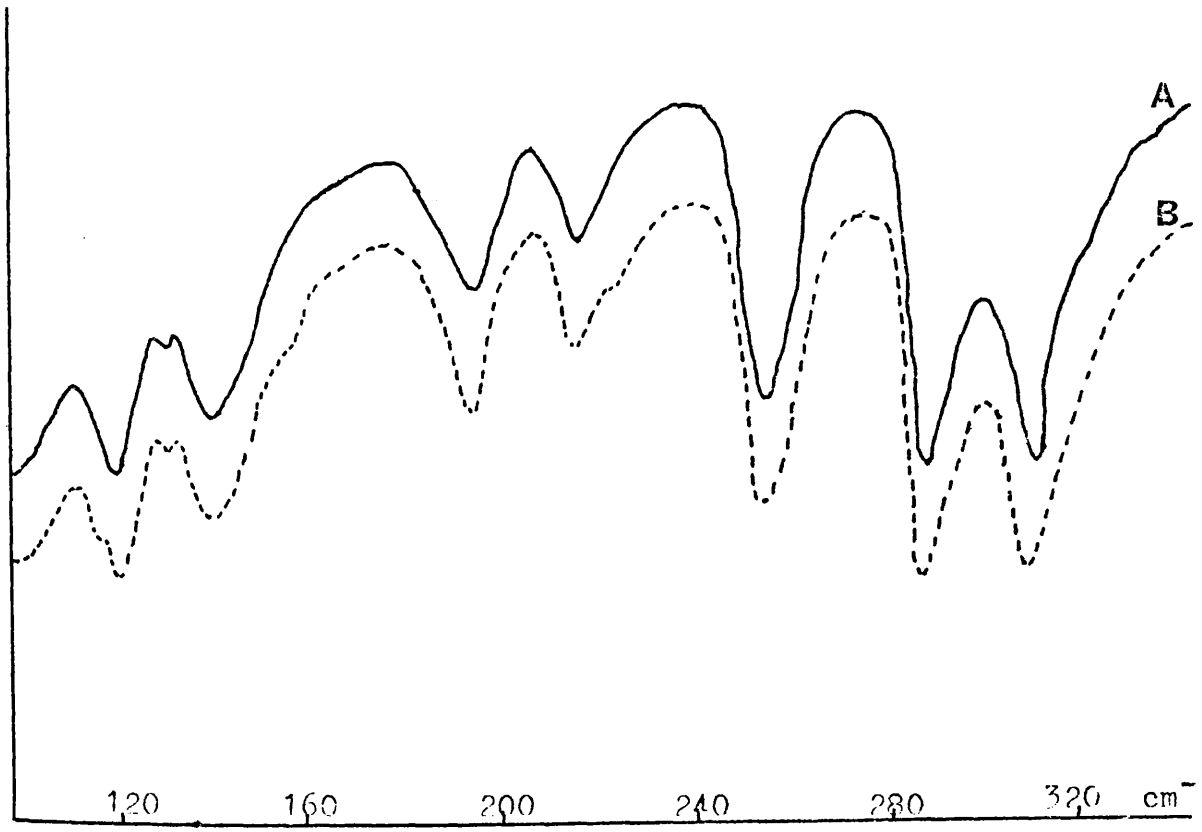
Full experimental details, atomic parameters, thermal parameters and structure factor tables are given in Appendix II.

Figures II. 13 and II. 14 show the atomic numbering scheme and the molecular packing. Table II. III gives interatomic dimensions and Table II. IV gives some least-squares best planes calculated through the molecule.

(c) Discussion

The analysis has revealed that $Zn(py)_2(NO_3)_2$ possesses a monomeric structure with the nitrate groups almost

FAR INFRARED SPECTRA OF $Zn(Py)_2(NO_3)_2$



A - Powder

B Crystals

Recorded at -196°C

FIGURE II.12

certainly unidentate and both identically asymmetric with respect to the zinc atom. The two pyridines and two shortest-bonded oxygen atoms N(3), N(4), O(2), O(4) adopt an approximate tetrahedral configuration. Except for the asymmetric nitrate groups, the overall molecular features of the complex are very similar to those of $(Me_3PO)_2Co(NO_3)_2$ [64] and the closest zinc-oxygen (Zn-O(2) 2.044(12) Å, Zn-O(4) 2.047(13) Å) and zinc-nitrogen distances (Zn-N(3) 2.016(12) Å, Zn-N(4) 2.048(12) Å) correspond with values for similar bonds in other complexes [171]. In the present molecule, the pyridine and nitrato-groups are staggered so as to minimise steric effects, and although the long zinc-oxygen distances are not expected to represent significant bonding interactions, it is probable that the relatively close approach of atoms O(1) and O(5) to the pyridine and nitrate groups has influenced the distortion of the complex from ideal tetrahedral geometry. This distortion is manifested in the values of 120.7(5)° and 96.3(5)° for the valency angles N(3)-Zn-O(2) and O(2)-Zn-O(4) respectively. In comparison, the structure of $Zn(py)_2(N_3)_2$ [172] has a much more regular tetrahedral geometry with the smaller steric requirements of the azide groups. The pyridine groups in the latter complex are also staggered with a dihedral angle between the pyridine planes of 80° while in $Zn(py)_2(NO_3)_2$ the corresponding value is 76°.

It has been suggested that a number of amine complexes of formula $M(L)_2(NO_3)_2$ (M = Co(II), Ni(II), Cu(II) and Zn(II), L = unidentate amine) have six-coordinate structures

similar to $(Me_3PO)_2Co(NO_3)_2$ with symmetrically bidentate nitrato-groups [173]. For phosphine oxide complexes of $Zn(NO_3)_2$ the situation is complicated. X-ray powder photographs have shown that the analogous zinc and cobalt nitrate complexes of trimethylphosphine oxide are not isostructural unlike the corresponding complexes of triphenylphosphine oxide [174]. However, it is reasonable to suppose that all of these complexes may contain nitrate groups which are more or less symmetrically bidentate. On this basis it might have been expected that $Zn(py)_2(NO_3)_2$ would display a closely related mode of nitrate coordination, which is not borne out by the results of the analysis. However, although it is difficult to assess the effects of crystal-packing forces on such complexes, the present structure suggests the possibility of two stable configurations for bis(ligand) complexes and zinc(II) nitrate. The first configuration, adopted in this instance, involves the use of zinc sp^3 hybrid orbitals with unidentate nitrate coordination, while the second would have bidentate nitrate groups and hence be six-coordinate utilising sp^3d^2 hybrid orbitals. Six-coordination would therefore involve the higher-energy 4d orbitals (or in M.O. terms, antibonding orbitals). For complexes or metals with incomplete 3d shells, there would seem to be no energy barrier to the overlap of two oxygen atoms of a bidentate nitrate group with two lobes of a d-type orbital. However, this is not the case for zinc where an energy balance will determine the choice of either six-coordination involving bidentate nitrate groups with 4d orbitals or alternatively,

of four-coordination with unidentate nitrate groups. It is therefore not surprising that the structure of the present molecule differs markedly from that of $Zn(py)_3(NO_3)_2$ [80, 81] (see Section II. 2 below) which is seven-coordinate by virtue of the two asymmetric bidentate nitrate groups, and in which the use of 4d orbitals is required for any configuration in which all the groups are coordinated. The difference is remarkable when it is considered that $Zn(py)_2(NO_3)_2$ may be prepared by the thermal decomposition of $Zn(py)_3(NO_3)_2$ [170, 145].

Prior to the present work, no other structures of $Zn(NO_3)_2$ complexes with ligands other than water have been reported. The structures of the hydrated salts $Zn(NO_3)_2 . nH_2O$ (n = 2 or 4) are known and they both contain six-coordinate zinc with the nitrate groups in the tetrahydrate unidentate [88] and in the dihydrate bridging [100]. Thus, although the complication of hydrogen-bonding is present, the nitrato-coordination in $Zn(NO_3)_2 . 4H_2O$ has the greatest interest for the present study. However, the structure of this salt has not been completed since it was assumed that it was isostructural with $Ni(NO_3)_2 . 4H_2O$ [88, 87] on the basis of space group and unit cell similarities. It would therefore be unreasonable to compare the asymmetry of the nitrate groups in the present complex with those in $Ni(NO_3)_2 . 4H_2O$ as many detailed differences in bond lengths have been found in other supposedly 'isostructural' complexes [81].

In fact, the asymmetry of the nitrate groups is

not large compared with many other complexes containing unidentate nitrate groups. Addison et al [36] have suggested that, for unidentate coordination, one metal-oxygen distance should be 0.8 - 1.1 Å longer than the other so that there can only be significant bonding with one oxygen atom of each nitrato-group. In the present complex, this difference in M-O distances is ca. 0.7 Å while in $[Cu(py)_2(NO_3)_2]_2$ py [75-6] (II.1.2) the corresponding values are 0.6 and 0.9 Å, and from bonding arguments the former complex was expected to contain unidentate nitrato-groups, while in the latter, the long M-O distances should represent significant interaction. Therefore, it is probably unreasonable to differentiate between unidentate and asymmetric bidentate bonding purely on the difference in M-O distances without consideration of the bonding potential of the metal concerned.

Within each nitrate group of $Zn(py)_2(NO_3)_2$ there is little significant variation in N-O bond lengths, and there is therefore no discernable polarisation effect. The O-N-O angles are very close to the ideal value of 120°, and there is again little apparent effect from the metal coordination. This lack of distortion of the nitrate groups was also found in $Zn(NO_3)_2.2H_2O$ [100] where the metal-nitrate interaction should be similar Zn-O = 2.02 Å; 2.22 Å (bridging). The values of 110.6(9)° and 112.4(10)° for the angles Zn-O(2)-N(1) and Zn-O(4)-N(2) respectively, agree well with the suggested [106] value of 110° for normal unidentate coordination. Both nitrate groups are virtually planar with the zinc atom slightly removed from each plane (Table II.IV) and moreover, the dihedral

angle between these planes (69^{o}) is comparable with the dihedral angle between the planes of the pyridine moieties (76^{o}).

In the crystal structure, all intermolecular contacts are equal to or greater than van der Waals distances. The distance of the oxygen atom, O(3), from its nearest zinc atom is 3.46 Å but this has little apparent effect on the nitrate dimensions.

The vibration frequencies of the nitrate group in $Zn(py)_2(NO_3)_2$ and $Zn(py)_3(NO_3)_2$ [130, 141, 145, 147, 170] are almost identical despite the completely different modes of coordination. In the far infrared region of the spectrum, there are marked differences with $Zn(py)_2(NO_3)_2$ showing two strong bands attributed to metal-oxygen frequencies at 305 and 285 cm^{-1}. These occur in the same region as has been found for other complexes which are expected to contain symmetrically bidentate nitrato-groups [145, 147] but these frequencies may be reconciled with the molecular structure by comparison with the two (M-X) frequencies obtained for the corresponding C_{2v} halide complexes which also occur around 300 cm^{-1} [175]. For $Zn(py)_3(NO_3)_2$, the highest frequency band attributable to a metal-oxygen vibration is at 210 cm^{-1} which is probably indicative of the weaker Zn-O bonding.

TABLE II.III

$Zn(py)_2(NO_3)_2$

Interatomic distances (Å) and angles (°) with estimated standard deviations in parentheses

(a) Interatomic distances

Zn(1)-O(1)	2.758(19)	C(6)-N(4)	1.43(2)
Zn(1)-O(2)	2.044(12)	C(6)-C(7)	1.41(3)
Zn(1)-O(4)	2.047(13)	C(7)-C(8)	1.39(3)
Zn(1)-O(5)	2.754(14)	C(8)-C(9)	1.48(2)
Zn(1)-N(3)	2.016(12)	C(9)-C(10)	1.38(3)
Zn(1)-N(4)	2.048(12)	C(10)-N(4)	1.35(2)
C(1)-N(3)	1.39(2)	N(1)-O(1)	1.28(2)
C(1)-C(2)	1.43(2)	N(1)-O(2)	1.28(2)
C(2)-C(3)	1.39(3)	N(1)-O(3)	1.27(2)
C(3)-C(4)	1.40(3)	N(2)-O(4)	1.31(2)
C(4)-C(5)	1.44(2)	N(2)-O(5)	1.25(2)
C(5)-N(3)	1.35(2)	N(2)-O(6)	1.25(2)

TABLE II.III (cont)

(b) Interbond angles

O(1)-Zn(1)-O(2)	52.2(5)	C(1)-N(3)-C(5)	118.5(13)
O(1)-Zn(1)-O(4)	75.3(5)	C(1)-N(3)-Zn(1)	120.9(10)
O(1)-Zn(1)-O(5)	113.9(5)	C(5)-N(3)-Zn(1)	120.6(11)
O(1)-Zn(1)-N(3)	87.2(6)	C(7)-C(6)-N(4)	120.5(16)
O(1)-Zn(1)-N(4)	148.8(5)	C(6)-C(7)-C(8)	119.8(16)
O(2)-Zn(1)-O(4)	96.3(5)	C(7)-C(8)-C(9)	119.2(17)
O(2)-Zn(1)-O(5)	147.1(5)	C(8)-C(9)-C(10)	117.6(17)
O(2)-Zn(1)-N(3)	120.7(5)	C(9)-C(10)-N(4)	123.5(14)
O(2)-Zn(1)-N(4)	96.6(5)	C(6)-N(4)-C(10)	119.1(13)
O(4)-Zn(1)-O(5)	51.4(5)	C(6)-N(4)-Zn(1)	119.6(10)
O(4)-Zn(1)-N(3)	114.7(5)	C(10)-N(4)-Zn(1)	121.3(9)
O(4)-Zn(1)-N(4)	111.7(5)	Zn(1)-O(1)-N(1)	77.0(11)
O(5)-Zn(1)-N(3)	83.6(5)	Zn(1)-O(2)-N(1)	110.6(9)
O(5)-Zn(1)-N(4)	91.7(5)	Zn(1)-O(4)-N(2)	112.4(10)
N(1)-Zn(1)-N(2)	108.2(4)	Zn(1)-O(5)-N(2)	80.1(9)
N(3)-Zn(1)-N(4)	114.4(5)	O(1)-N(1)-O(2)	119.4(16)
C(2)-C(1)-N(3)	119.1(16)	O(1)-N(1)-O(3)	120.1(16)
C(1)-C(2)-C(3)	121.2(18)	O(2)-N(1)-O(3)	120.5(14)
C(2)-C(3)-C(4)	120.4(15)	O(4)-N(2)-O(5)	116.1(13)
C(3)-C(4)-C(5)	116.0(16)	O(4)-N(2)-O(6)	123.5(14)
C(4)-C(5)-N(3)	124.7(15)	O(5)-N(2)-O(6)	120.4(14)

TABLE II.III (cont)

(c) Intramolecular non-bonded distances

Zn(1). . .C(1)	2.98	O(2). . .O(3)	2.21
Zn(1). . .C(5)	2.94	O(2). . .O(4)	3.05
Zn(1). . .C(6)	3.02	O(2). . .N(4)	3.06
Zn(1). . .C(10)	2.98	O(4). . .O(5)	2.18
Zn(1). . .N(1)	2.77	O(4). . .O(6)	2.25
Zn(1). . .N(2)	2.82	O(4). . .N(1)	3.25
O(1). . .C(5)	3.22	O(4). . .N(4)	3.39
O(1). . .O(2)	2.21	O(5). . .C(10)	3.28
O(1). . .O(3)	2.21	O(5). . .O(6)	2.17
O(1). . .O(4)	2.99	O(5). . .N(3)	3.23
O(1). . .N(3)	3.34	O(5). . .N(4)	3.48
O(2). . .C(6)	3.13		

TABLE II.III (cont)

(d) Intermolecular distances

Zn(1). . .O(3)^{I}	3.46	O(4). . .C(4)^{IV}	3.52
O(2). . .C(1)^{II}	3.47	O(4). . .C(5)^{IV}	3.51
O(2). . .C(6)^{II}	3.30	O(5). . .C(3)^{V}	3.32
O(2). . .O(3)^{I}	3.28	O(5). . .O(5)^{VI}	3.40
O(2). . .N(4)^{II}	3.57	O(6). . .C(3)^{VII}	3.53
O(3). . .C(1)^{II}	3.25	O(6). . .C(4)^{VII}	3.36
O(3). . .C(6)^{II}	3.26	O(6). . .C(4)^{IV}	3.57
O(3). . .C(8)^{III}	3.40	O(6). . .C(9)^{VI}	3.50
O(3). . .C(9)^{III}	3.45	O(6). . .C(10)^{VI}	3.56
O(3). . .N(3)^{II}	3.46	N(1). . .C(6)^{II}	3.48
O(3). . .N(4)^{II}	3.54		

Roman numerals as superscripts refer to the following equivalent positions with respect to the reference molecule at x, y, z.

I	-1/2 + x, 1/2 - y, -1/2 + z
II	1/2 + x, 1/2 - y, 1/2 + z
III	1 + x, y, z
IV	1 - x, -y, 1 - z
V	-x, -y, -z
VI	-x, -y, 1 - z
VII	x, y, 1 + z

TABLE II.IV

$Zn(py)_2(NO_3)_2$

Least-squares best planes through the molecule. The equations are in the form $k\underline{X}' + \ell\underline{Y}' + m\underline{Z}' = n$, where $\underline{X}'$, $\underline{Y}'$ and $\underline{Z}'$ are coordinates in Å. Distances of atoms from planes (Å) are given in square brackets.

	$\underline{k}$	$\underline{\ell}$	$\underline{m}$	$\underline{n}$
Plane(1):				
C(1)-(5), N(3)	0.4943	0.7517	-0.4366	1.8635
C(1) 0.003, C(2) -0.011, C(3) 0.002, C(4) 0.014, C(5) -0.023, N(3) 0.015, Zn(1) 0.065				
Plane(2):				
C(6)-(10), N(4)	-0.5196	0.1912	-0.8327	2.9140
C(6) 0.018, C(7) 0.002, C(8) -0.026, C(9) 0.032, C(10) -0.014, N(4) -0.012, Zn(1) -0.099				
Plane(3):				
O(1)-(3), N(1)	-0.1821	0.4715	-0.8629	-1.2750
O(1) 0.005, O(2) 0.005, O(3) 0.005, N(1) -0.015, Zn(1) -0.291				
Plane(4):				
O(4)-(6), N(2)	0.3755	-0.5090	-0.7745	-2.3475
O(4) -0.001, O(5) -0.001, O(6) -0.001, N(2) 0.003, Zn(1) -0.129				

Dihedral angles (°) between planes

Plane (1)-(2)	75.5	Plane (2)-(3)	25.4
Plane (1)-(3)	50.1	Plane (2)-(4)	69.4
Plane (1)-(4)	81.9	Plane (3)-(4)	68.9

FIGURE II.12

$Zn(py)_2(NO_3)_2$

A view of the molecule along b showing the atomic numbering

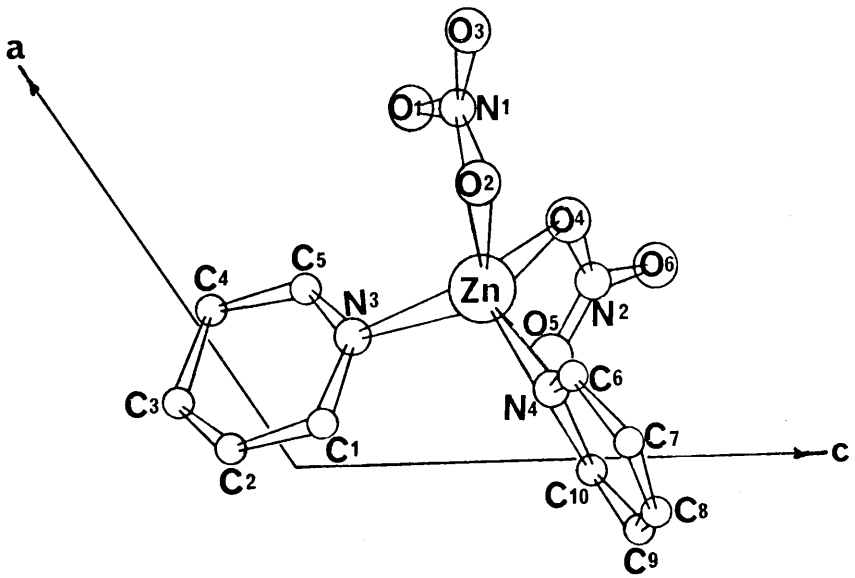
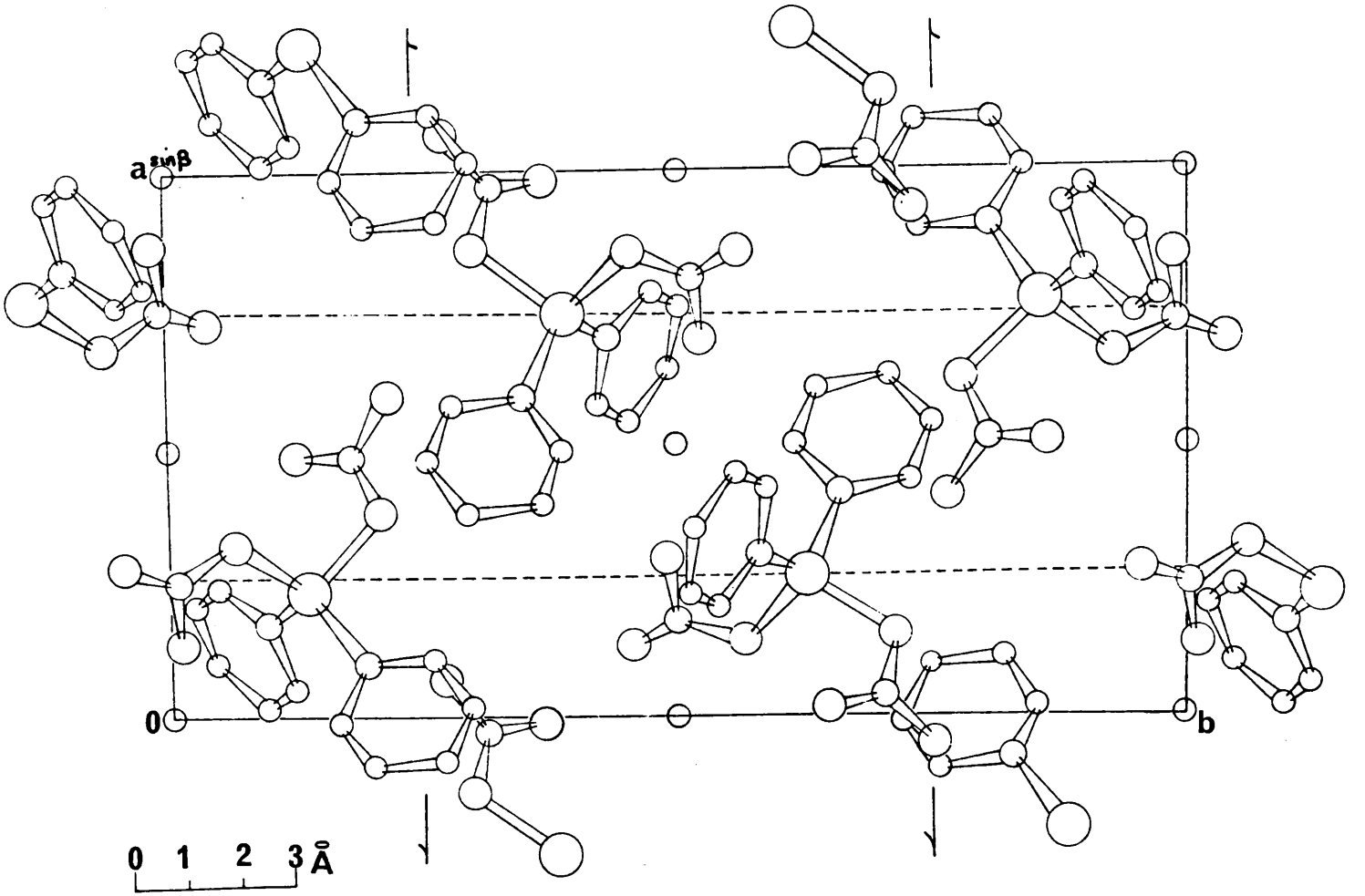

a
O3
O1
N1
O2
O4
O6
C4
C5
N3
Zn
O5
N2
C6
C3
N4
C7
C1
c
C2
C10
C8
C9

FIGURE II.14

$Zn(py)_2(NO_3)_2$

The molecular packing viewed along the c axis


a sinβ
0
b
0 1 2 3 Å

II. 1. 5. PYRIDINE COMPLEXES OF $Co(NO_3)_2$, $Ni(NO_3)_2$ AND $Cd(NO_3)_2$

Pyridine does not form such extensive series with the nitrates of Co(II) and Ni(II) as previously found for Cu(II) [126] and Zn(II) [170]. In a thermogravimetric analysis examination of the $M(NO_3)_2$ (M = Co(II) or Ni(II)) systems with pyridine [176] only two separate phases were isolated for each metal: $M(py)_3(NO_3)_2$ and $M(py)_6(NO_3)_2$. However, a corresponding study of pyridine adducts of $Cd(NO_3)_3$ [170] showed the existence of three phases: $Cd(py)_3(NO_3)_2$, $Cd(py)_6(NO_3)_2$ and $Cd_2(py)_3(NO_3)_4$. There have been no reports of tetrakis-pyridine complexes of these metal(II) nitrates and, although $Co(py)_2(NO_3)_2$ was reported in one study [177], all subsequent attempts to prepare anhyrous bis-pyridine complexes in the solid state have failed. In solution, bis-pyridine complexes have been postulated [176, 178, 179], but these species are probably solvated and the only compounds isolated in the solid state are the dihydrates, $Co(py)_2(NO_3)_2 \cdot 2H_2O$ and $Ni(py)_2(NO_3)_2 \cdot 2H_2O$.

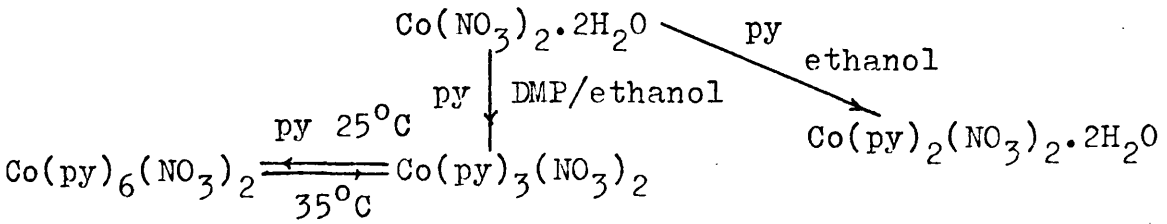
Interrelation diagrams of the three systems are shown in Figure II. 15 and the individual complexes are discussed below.

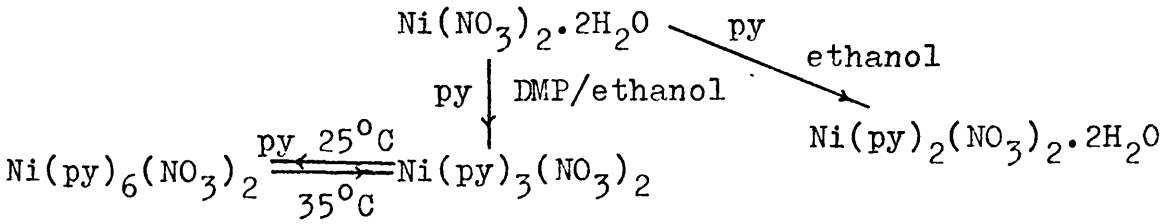
(a) $M(py)_3(NO_3)_2$ (M = Co(II), Ni(II), Cd(II))

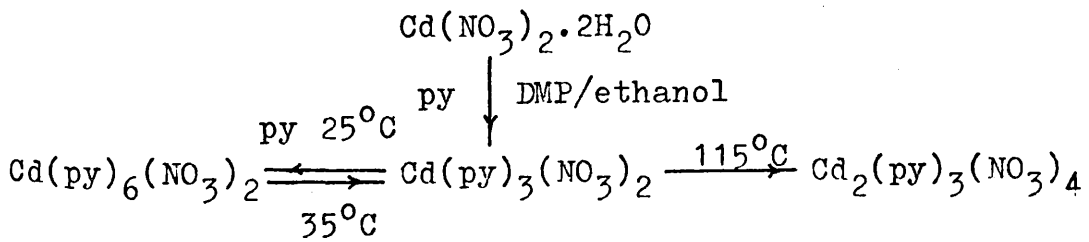
These complexes are discussed in Section II. 2.

FIGURE II.15

Interrelationship diagrams for the systems $M(NO_3)_2.nH_2O$-pyridine (M = Co^{II}, Ni^{II}, Cd^{II})







(b) $M(py)_6(NO_3)_2$ (M = Co(II), Ni(II), Cd(II))

The infrared spectra of all three complexes indicate that the nitrate groups are coordinated but that free and coordinated pyridine is present. The far infrared spectra of the hexakis and tris-pyridine complexes of cobalt(II) and nickel(II) nitrates respectively are almost identical [141, 145] and a thermogravimetric study [176] indicates that the complexes are best formulated as $[M(py)_3(NO_3)_2]$ 3py. Similar remarks probably also apply to the cadmium hexakis-pyridine complex but this was more difficult to analyse because of rapid loss of pyridine from the sample [170].

(c) $Cd_2(py)_3(NO_3)_4$

This complex was originally prepared by the thermal decomposition of $Cd(py)_3(NO_3)_2$ [170] but attempts to obtain crystals of this species have so far proved unsuccessful. Ouellette and Haendler [170] have suggested that complexes in the cadmium(II) nitrate-pyridine system have polymeric, distorted octahedral geometries with bridging through the nitrate groups. However, this is based on fairly tenuous evidence and the actual mode of bridging is by no means certain. Moreover, the stereochemistry around the cadmium is not easy to predict as examples of 4-, 6-, 7- and 8-coordination are known for this metal and discussion is better left until an X-ray examination can be undertaken.

(d) $M(py)_2(NO_3)_2 \cdot 2H_2O$ (M = Co(II), Ni(II))

Infrared studies [130] of these complexes have shown that all of the groups are coordinated in each case but the detailed modes of nitrate coordination were not clear. A preliminary X-ray examination of the nickel(II) complex revealed extremely intense diffraction patterns suggesting a high degree of intermolecular association. Since few examples of this type of complex have been reported, a three-dimensional X-ray analysis was carried out to study the effect of both coordinated water molecules and another ligand on the detailed nitrate coordination.

II.1.6 CRYSTAL AND MOLECULAR STRUCTURE OF DIAQUO[BUSNITRAMOBIS(PYRIDINE)]-NICKEL(II)

II.1.6. CRYSTAL AND MOLECULAR STRUCTURE OF DIAQUO [BIS-NITRATOBIS(PYRIDINE)] -NICKEL(II), $Ni(py)_2(NO_3)_2(H_2O)_2$

(a) Material Used in the Determination

The original preparation of this compound [180] produced satisfactory crystals for the X-ray determination.

(b) Experimental and Results

Full experimental details, atomic parameters, thermal parameters and structure-factor tables are given in Appendix III.

Figures II.16 and II.17 show the atomic numbering scheme and the molecular packing respectively. Table II.V lists interatomic dimensions and Table II.VI gives some least-squares best planes calculated through the molecule.

(c) Discussion

The analysis has revealed a monomeric six-coordinate structure and, because the nickel atom is constrained to lie on a crystallographic centre of inversion, the octahedron is formed from symmetry-related pairs of oxygen atoms from water molecules O(4), O'(4) and nitrate groups O(1), O'(1), and of nitrogen atoms from the pyridine moieties N(2), N'(2) (Figure II.16). The octahedron around the nickel is distorted (Figure II.18) but it is

difficult to assess the relative importance of crystal packing and steric effects of the nitrate groups on this distortion. Probably the predominant factor will be the intermolecular hydrogen-bond network as a similar order of distortion of the nickel coordination occurs with $Ni(NO_3)_2 \cdot 4H_2O$ [87] which also has a hydrogen-bonding system in the crystal.

The nitrate groups are monodentate and the nickel-ligand bond lengths (Ni-O(1) 2.101(2), Ni-O(4) 2.061(2), Ni-N(2) 2.095(2) Å) agree well with reported values in other complexes [181]. The dimensions of the pyridine ring are also in agreement with literature values [169].

The high stability of the crystals and the ability to produce extremely intense diffraction patterns after relatively short exposure to X-rays, had initially led us to expect that within the crystal there existed some form of intermolecular association other than normal van der Waals contacts. An examination of the crystal packing, reveals a complex system of O . . . O hydrogen bonding extending throughout the crystal. Each coordinated water molecule is hydrogen bonded to two nitrate groups, one on each of <u>two</u> neighbouring complex molecules, the O . . . O distances being 2.87 and 2.76 Å, (Figure II.17). Thus each molecule of the complex is hydrogen bonded to its neighbours both through its water and nitrate groupings, giving rise to a total of eight hydrogen bonds per molecule. A similar type of hydrogen bonding is reported in $Ni(NO_3)_2(H_2O)_4$ [87], in which the O . . . O contacts are 2.80 and 2.91 Å, values very

close to those of the present complex although the molecular structures differ in that the nitrate groups of the tetrahydrate salt occupy cis positions, whereas they occupy trans positions in the present bis (pyridine) molecule. A further difference between these two crystal structures is that, in the present complex, the hydrogen bonding is approximately aligned in the bc-plane, whilst in the salt, there is no such regular arrangement. Hydrogen bonding also probably plays a part in the crystal structure of $Ni(NO_3)_2(H_2O)_2$ [99] with O . . . O contacts of 2.72 and 2.87 Å (distances calculated from atomic coordinates and unit cell dimensions) although in this case, each nickel atom bridges to four surrounding molecules through the nitrate groups, so that the overall structure is particularly rigid.

An interesting comparison can be made of the detailed mode of nitrate coordination in $Ni(py)_2(NO_3)_2(H_2O)_2$ and in the complexes $[Cu(py)_2(NO_3)_2]_2.py$ [75, 76] (II.1.2) $Zn(py)_2(NO_3)_2$ [96] (II.1.4) and $Ni(NO_3)_2(H_2O)_4$ [87]. The relevant bond lengths and angles are shown in Table II.VII. In all of these cases the nitrate groups are asymmetrically disposed to the metal atom and the asymmetry can be related to the angle made by the metal and nitrogen atoms with the strongest bound oxygen atom (M-O(1)-N). It has been suggested that for normal monodentate coordination this angle should be close to 110^o [106]. This is realised in $Zn(py)_2(NO_3)_2$ [96] in which, although the longer Zn-O contacts are ca. 2.75 Å, consideration of the zinc orbitals likely to be employed in the bonding system supports the view that the

nitrate groups are monodentate. In $[Cu(py)_2(NO_3)_2]_2 \cdot py$ [75, 76], the nitrate groups are not equivalent and while one is expected to be a genuine asymmetric bidentate nitrate group, in the other, the metal-oxygen distance of 2.906 Å can represent at best a very weak interaction. The corresponding long Ni-O distance (3.24 Å) in the present complex is therefore not expected to represent significant interaction and moreover, this distance is of the same order as the long Ni-O contacts in $Ni(NO_3)_2(H_2O)_4$ [87] (3.11, 3.15 Å). The Ni-O(1)-N valency angles in the latter two complexes (present complex, 127.0(2)°; $Ni(NO_3)_2(H_2O)_4$, 122.4(7)°, 125.4(7)°) are extended from the normal values found in $Zn(py)_2(NO_3)_2$ as a result of the hydrogen bonding, the nitrate groups being held in a slightly "extended" attitude by virtue of their close association with neighbouring molecules. The effects of hydrogen bonding are also manifested in the N-O bond lengths and O-N-O bond angles. Polarisation by the nickel atom might have been expected to make the N(1)-O(3) bond shorter than the N(1)-O(1) bond, whereas, in the present complex these bonds are approximately the same length. In $Ni(NO_3)_2(H_2O)_4$, the different N-O distances between the two nitrate groups reflect the non-equivalence of the hydrogen bonding since in one nitrate group [4(a)] two oxygens [O(3) and O(2)] are involved in hydrogen bonds whereas, in the other [4(b)] only the terminal oxygen atom [O(3)] is involved. The latter case parallels the situation in the present complex and indeed, the variation in N-O bond lengths are very similar. If the angles in the nitrate

groups are compared, the largest O-N-O angle might have been expected opposite the shortest Ni-O distance, but the hydrogen bonding has also distorted this view.

Another feature of interest of the crystal packing is that the aromatic planes of all the pyridine moieties are aligned in one direction throughout the crystal, while the delocalised nickel-nitrate inorganic sheets are all aligned in another direction. A related arrangement has also been found in the trimeric nickel complex $[Ni(\beta\text{-pic})_2(NO_2)_2]_3$ [151] and it was suggested in this case that this was a factor in determining the molecular stability. It is probable that such alignment of delocalised planes is also a factor in the crystal-stability of the present compound. This feature is also present in the crystal structures of the two forms of $Cu(\alpha\text{-pic})_2(NO_3)_2$ [77-9] (III. 1) and in the molecular structure of $[Cu(py)_2(NO_3)_2]_2 \cdot py$ [75, 76] (II. 1. 2) although in the latter complex the planes do not extend throughout the crystal. Despite this feature however, the analysis suggests that the coordinated water molecules have played a vital role in the existence of the present complex as a crystalline species, and have contributed to the ease of formation.

TABLE II.V

$Ni(py)_2(NO_3)_2(H_2O)_2$

Interatomic distances (Å) and angles (°) with estimated standard deviations in parentheses

(a) Bonded distances

Ni(1)-O(1)	2.101(2)	C(4)-C(5)	1.385(5)
Ni(1)-O(4)	2.061(2)	C(5)-N(2)	1.340(4)
Ni(1)-N(2)	2.095(3)	N(1)-O(1)	1.267(3)
C(1)-C(2)	1.377(5)	N(1)-O(2)	1.232(4)
C(1)-N(2)	1.341(5)	N(1)-O(3)	1.258(3)
C(2)-C(3)	1.390(5)	Mean C-C	1.381
C(3)-C(4)	1.375(6)	Mean C-N	1.340
C(1)-H(1)	0.99(5)	C(5)-H(5)	0.90(4)
C(2)-H(2)	1.00(5)	O(4)-H(6)	0.85(5)
C(3)-H(3)	1.00(6)	O(4)-H(7)	0.72(6)
C(4)-H(4)	0.98(6)	Mean C-H	0.97
		Mean O-H	0.78

TABLE II.V (cont)

(b) Interbond angles

O(1)-Ni(1)-N(2)	93.11(1)	C(1)-C(2)-C(3)	118.9(4)
O(1)-Ni(1)-O(4)	83.3(1)	C(2)-C(3)-C(4)	118.2(4)
O(1)-Ni(1)-N'(2)	86.9(1)	C(3)-C(4)-C(5)	119.3(4)
O(1)-Ni(1)-O'(4)	96.7(1)	C(4)-C(5)-N(2)	123.0(3)
N(2)-Ni(1)-O(4)	87.7(1)	Ni(1)-O(1)-N(1)	127.0(2)
N(2)-Ni(1)-O'(4)	92.4(1)	O(1)-N(1)-O(2)	121.6(3)
Ni(1)-N(2)-C(1)	120.0(2)	O(1)-N(1)-O(3)	117.4(3)
Ni(1)-N(2)-C(5)	122.9(2)	O(2)-N(1)-O(3)	121.0(3)
C(1)-N(2)-C(5)	117.1(3)	Mean C-C-C	118.8
N(2)-C(1)-C(2)	123.4(3)	Mean C-C-N	123.2
N(2)-C(1)-H(1)	116(3)	C(4)-C(5)-H(5)	121(3)
C(2)-C(1)-H(1)	120(3)	N(2)-C(5)-H(5)	116(3)
C(1)-C(2)-H(2)	117(3)	H(6)-O(4)-H(7)	99(5)
C(3)-C(2)-H(2)	124(3)	O'(3)-O(4)-O"(3)	100.0(1)
C(2)-C(3)-H(3)	121(3)	O'(4)-O(3)-O"(4)	118.9(1)
C(4)-C(3)-H(3)	121(3)	O(4)-H(6)-O'(3)	151(2)
C(3)-C(4)-H(4)	124(3)	O(4)-H(6)-O"(3)	166(2)
C(5)-C(4)-H(4)	117(3)		
		Mean C-C-H	121
		Mean N-C-H	116

TABLE II.V (cont)

(c) Intermolecular distances for non-hydrogen atoms

Ni(1). . .C(1)	3.00	O(1). . .N(2)	3.05
Ni(1). . .C(5)	3.04	O(2). . .C(1)	3.28
Ni(1). . .O(2)	3.24	O(2). . .O(3)	2.17
Ni(1). . .N(1)	3.04	O(2). . .O'(4)	3.02
O(1). . .C(1)	3.18	O(2). . .N'(2)	3.17
O(1). . .C'(5)	3.03	O(4). . .C(1)	3.09
O(1). . .O(2)	2.18	O(4). . .C'(5)	3.30
O(1). . .O(3)	2.16	O(4). . .N'(1)	3.39
O(1). . .O'(4)	3.11	O(4). . .N(2)	2.88
O(1). . .N'(2)	2.89	N(1). . .N(2)	3.46

TABLE II.V (cont)

(d) Intermolecular contacts including those involved in hydrogen bonding

O(1). . .O(3)^{I}	3.28	O(3). . .C(2)^{V}	3.36
O(1). . .O(4)^{II}	3.34	O(3). . .C(3)^{V}	3.31
O(2). . .C(4)^{III}	3.25	O(3). . .O(4)^{II}	2.76
O(2). . .C(5)^{III}	3.40	O(3). . .O(4)^{VI}	2.87
O(2). . .O(2)^{IV}	2.90	O(3). . .H(6)^{VI}	2.09
O(2). . .O(3)^{IV}	3.13	O(3). . .H(7)^{II}	2.06
O(2). . .N(1)^{IV}	3.01	O(4). . .N(1)^{I}	3.50

Roman numerals as superscripts refer to the following equivalent positions with respect to the reference molecule at x, y, z.

I	x, 1/2 - y, -1/2 + z
II	x, 1/2 - y, 1/2 + z
III	x, -1/2 - y, 1/2 + z
IV	-x, -y, 1 - z
V	1 - x, -y, 1 - z
VI	x, y, 1 + z

TABLE II.VI

$Ni(py)_2(NO_3)_2(H_2O)_2$

Least-squares best planes through the molecule. The equations are in the form $k\underline{X}' + \ell\underline{Y}' + m\underline{Z}' = n$, where $\underline{X}'$, $\underline{Y}'$ and $\underline{Z}'$ are coordinates in Å. Distances of atoms from planes (Å) are given in square brackets.

	$\underline{k}$	$\underline{\ell}$	$\underline{m}$	$\underline{n}$
Plane(1):				
O(1)-(3), N(1)	0.9468	0.0874	-0.3097	0.2159
O(1) 0.001, O(2) 0.001, O(3) 0.001, N(1) -0.004, Ni(1) -0.216				
Plane(2):				
C(1)-(5), N(2)	0.0933	0.1821	0.9788	-0.0131
C(1) 0.005, C(2) -0.003, C(3) -0.001, C(4) 0.004, C(5) -0.003, N(2) -0.001, Ni(1) 0.013				
Plane(3):				
O(4), H(6)-(7)	0.9745	-0.0118	-0.2240	1.1306
O(4) 0.000, H(6) 0.000, H(7) 0.000, Ni(1) -1.13				

Dihedral angles (°) between planes

Plane (1)-(2)	66
Plane (1)-(3)	8
Plane (2)-(3)	72

FIGURE II.16

$Ni(py)_2(NO_3)_2(H_2O)_2$

A view of the molecule along b showing the atomic numbering

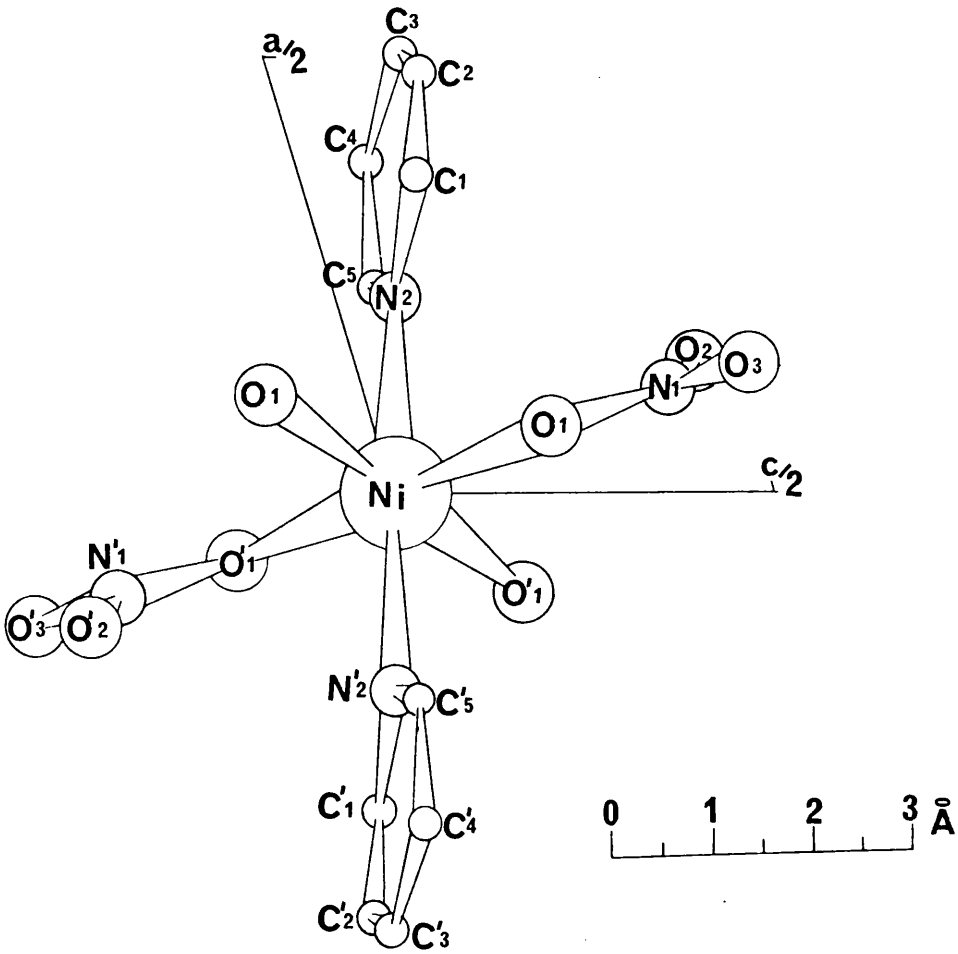
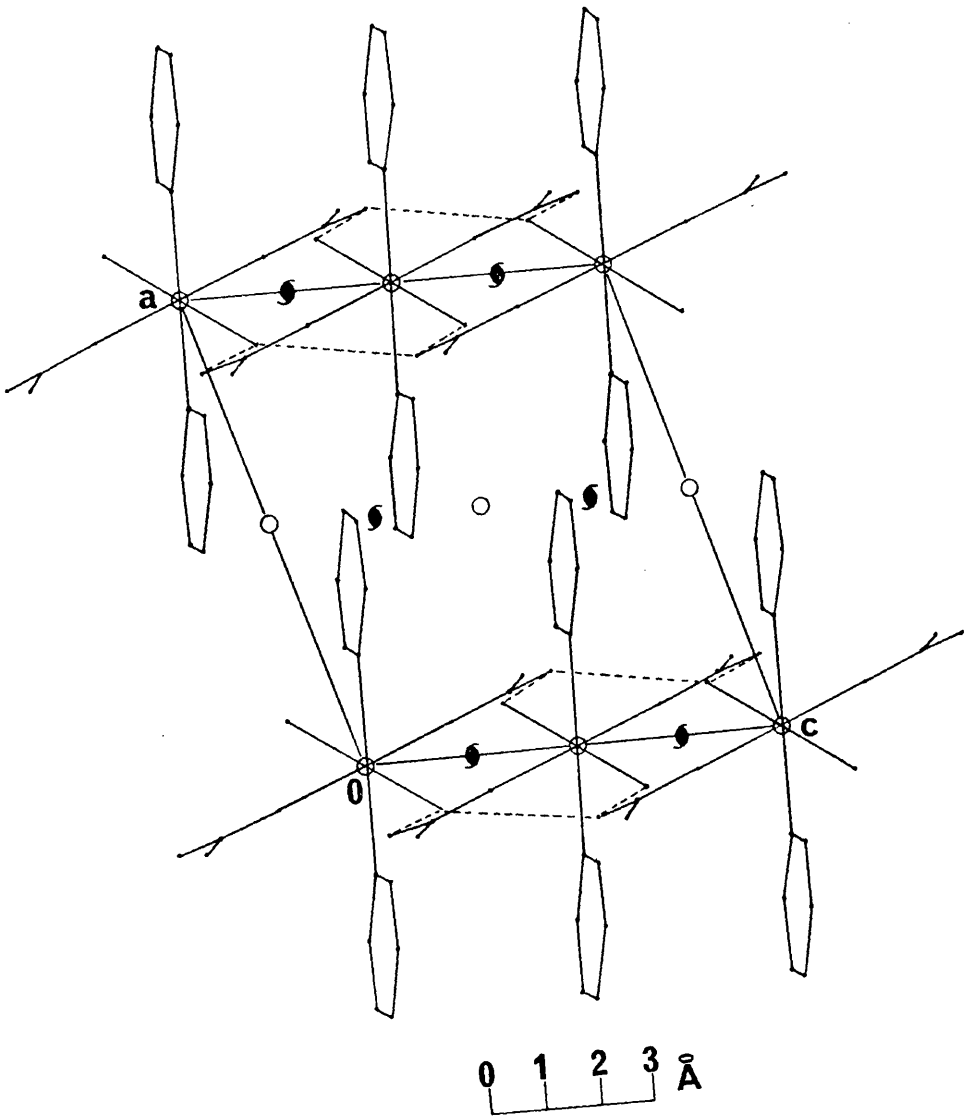

C3
a/2
C2
C4
C1
C5
N2
O2
O3
N1
O1
O1
c/2
Ni
N'1
O'1
O'1
O'3
O'2
N'2
C'5
C'1
C'4
C'2
C'3
0
1
2
3
Å

FIGURE II.17

$Ni(py)_2(NO_3)_2(H_2O)_2$

The molecular packing viewed along the b axis


a
c
0
0 1 2 3 Å

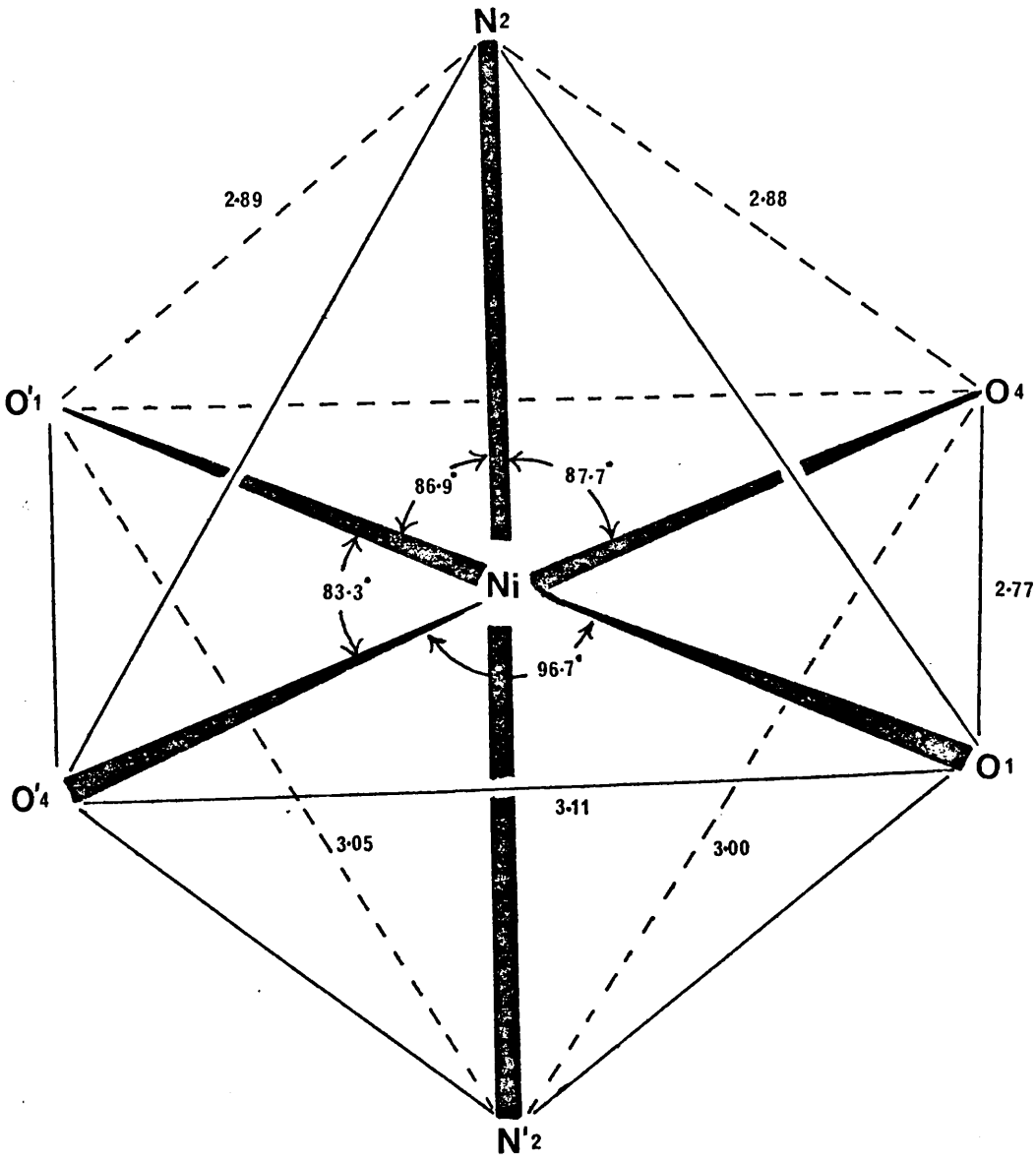
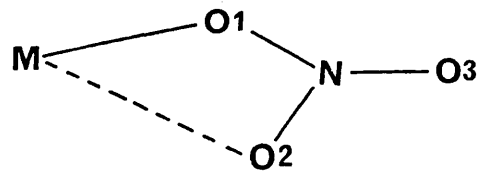


FIGURE II.18

The environment around the nickel in $Ni(py)_2(NO_3)_2(H_2O)_2$



	M-0(1)	M-0(2)	N-0(1)	N-0(2)	N-0(3)	0(1)M0(2)	M0(1)N	M0(2)N	0(1)N0(2)	0(1)N0(3)	0(2)N0(3)
1.	2.035(6)	2.618(8)	1.327(10)	1.261(11)	1.216(11)	55.3(3)	105.8(5)	80.7(5)	118.1(7)	117.1(8)	124.5(9)
	2.042(6)	2.906(7)	1.364(9)	1.228(10)	1.227(12)	50.0(2)	114.0(5)	76.5(5)	119.0(7)	116.3(8)	124.7(5)
2.	2.044(12)	2.758(19)	1.28(2)	1.28(2)	1.27(2)	52.2(5)	110.6(9)	77.0(11)	119.4(16)	120.1(16)	120.5(14)
	2.047(13)	2.754(14)	1.31(2)	1.25(2)	1.25(2)	51.4(5)	112.4(10)	80.1(9)	116.1(13)	120.4(14)	123.5(14)
3.	2.101(2)	3.244(3)	1.267(3)	1.231(4)	1.258(3)	41.7(1)	127.0(2)	69.4(2)	121.6(3)	117.4(3)	121.0(3)
4.	2.052(9)	3.151(9)	1.30(1)	1.25(1)	1.21(1)	43.5(4)	125.4(7)	72.6(7)	117.9(10)	118.1(10)	124.0(10)
	2.079(9)	3.109(9)	1.30(1)	1.24(1)	1.26(1)	45.0(4)	122.4(7)	71.6(7)	120.3(10)	118.6(10)	121.1(10)

1. Cu py_2 $(NO_3)_2$ $_2$ py
2. Zn py_2 $(NO_3)_2$
3. Ni py_2 $(NO_3)_2 . 2H_2O$
4. Ni $(NO_3)_2$ $(H_2O)_4$

TABLE II. VII

CHAPTER 2

Tris-pyridine Metal-Nitrato Complexes

II. 2. 1. INTRODUCTION

Divalent metal nitrates form tris-pyridine complexes fairly readily and, apart from the copper(II) nitrate-pyridine system, this is generally the easiest phase to obtain from solution. The molecular geometries of these species have been the subject of much speculation but spectroscopic studies have not produced conclusive results either of the metal ion configuration or on the mode of nitrate bonding present. The work carried out on individual complexes prior to the present X-ray examination is summarised below.

$Zn(py)_3(NO_3)_2$

The infrared spectrum of this complex was reported in 1966 by Frank and Rogers [130] but they did not postulate any structure. Ouellette and Haendler [170] using infrared and conductivity measurements suggested an octahedral structure with bridging nitrate groups although they did not rule out the possibility of a tetranitrato complex, $[Zn(py)_6][Zn(NO_3)_4]$, similar to those suggested by Addison for dimethylsulphoxide complexes of cadmium nitrate [182]. A far infrared examination [141, 145] led to speculation that the metal-nitrate interaction was weaker in the

tris-pyridine complex than had been found in the structure of $Zn(py)_2(NO_3)_2$ [96].

$Co(py)_3(NO_3)_2$

The cobalt(II) nitrate-pyridine system was examined by Ferraro et al [177] but no structural predictions were made. Later workers prepared $Co(py)_3(NO_3)_2$ and suggested it had an essentially octahedral structure containing both unidentate and bidentate nitrate groups [176, 178, 179]. A polymeric structure was not favoured because of the solubility of the complex in non-polar solvents.

Rosenthal et al [179] have examined the electronic spectrum and magnetic properties of $Co(py)_3(NO_3)_2$ in the solid state and in solution. They ruled out the possibility of a tetranitrato complex, $[Co(py)_6]\ Co(NO_3)_4$, from the absence of characteristic bands for $Co(NO_3)_4^{2-}$ [183] in the electronic spectrum. Therefore, these workers also favoured an octahedral structure with unidentate and bidentate nitrate groups.

$Ni(py)_3(NO_3)_2$

This complex was examined by the same groups of workers that studied the cobalt(II) nitrate-pyridine system [176, 178], and $Ni(py)_3(NO_3)_2$ was expected to have a very similar structure to $Co(py)_3(NO_3)_2$.

The properties of the tris-pyridine complexes of

cobalt(II) and nickel(II) nitrates in dichloromethane are of interest as both lose one molecule of pyridine to form $M(py)_2(NO_3)_2$ (M = Co(II) or Ni(II)), although this species cannot be isolated in the solid state. However, it was not possible to put any structural interpretation on this property.

$Cu(py)_3(NO_3)_2$

This was originally reported by two groups of workers [131, 132]. However, at a later date Haendler et al [126] challenged the existence of the complex as a separate phase and suggested that it was instead a mixture of $Cu(py)_4(NO_3)_2$ and $Cu(py)_2(NO_3)_2$, as they were unable to find any evidence for $Cu(py)_3(NO_3)_2$ in the thermal decomposition curve of the tetrakis-pyridine complex. Further studies [140, 141, 145] have shown that if $Cu(py)_4(NO_3)_2$ is recrystallised from various solvents, the tris-pyridine complex may be obtained but, although its infrared spectrum has been examined, no definite structure was suggested.

$Cd(py)_3(NO_3)_2$

This complex was prepared by Haendler et al [170] who recorded its infrared spectrum and conductivity in various solvents. They reported a molecular weight in excess of 7000 in dimethylformamide for $Cd(py)_3(NO_3)_2$ and suggested a polymeric distorted octahedral geometry with bridging through the nitrate groups.

Some of the suggested and possible structures for $M(py)_3(NO_3)_2$ (M = Co(II), Ni(II), Cu(II), Zn(II) and Cd(II)) are shown in Figure II. 20 and X-ray structural determinations were carried out to determine the most favourable configuration for this type of complex and also to obtain more information on the metal-nitrate bond.

Preliminary Experimental

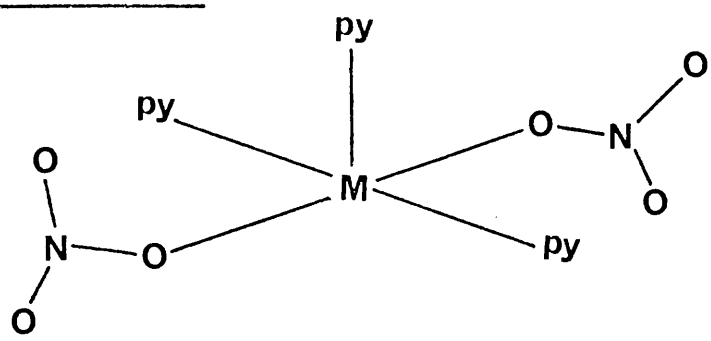
X-ray photographs of $M(py)_3(NO_3)_2$ (M = Co(II), Cu(II), Zn(II) and Cd(II)) indicate that all four complexes crystallise in space group C2/c (or Cc). However, $Ni(py)_3(NO_3)_2$ proved to be an exception to this and a study of poor-quality crystals of this complex suggested a triclinic cell to be appropriate. Unfortunately, it has not proved possible to obtain crystals of the latter complex which would be suitable for data collection.

Unit cell dimensions for $M(py)_3(NO_3)_2$ (M = Co(II), Cu(II) and Zn(II)) were found to be almost identical and a comparison of intensities of equivalent reflexions from Weissenberg photographs indicated that these three complexes were apparently isomorphous. The surprising nature of this result, particularly for the copper complex, led to the independent determinations of the complete structure of each species.

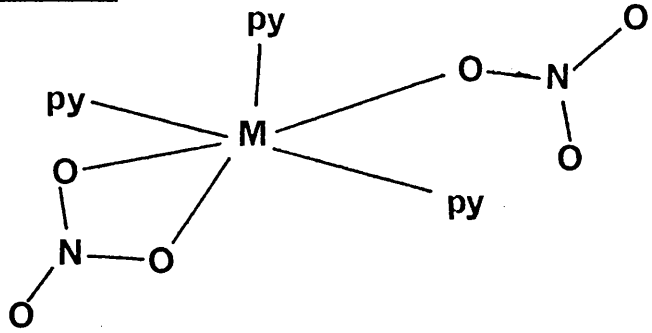
The unit cell of the cadmium complex was larger and no direct equivalence of intensities with those of the above three complexes was discernable. As it had been predicted that

$Cd(py)_3(NO_3)_2$ was a polymeric species [170], the structure of this complex was solved to determine how the configuration around the cadmium compared with the geometries of the other tris-pyridine complexes.

A 5-Coordinate



B 6-Coordinate



C Polymeric Distorted Octahedral

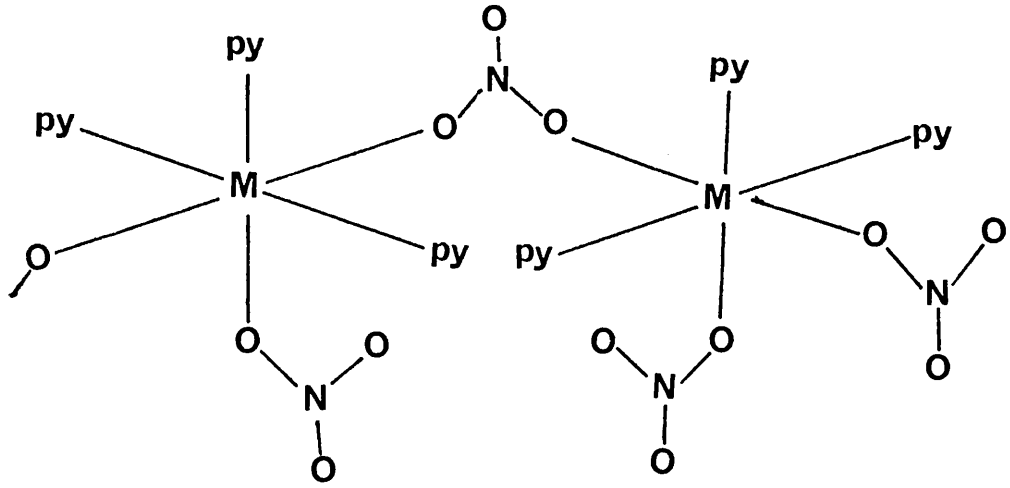
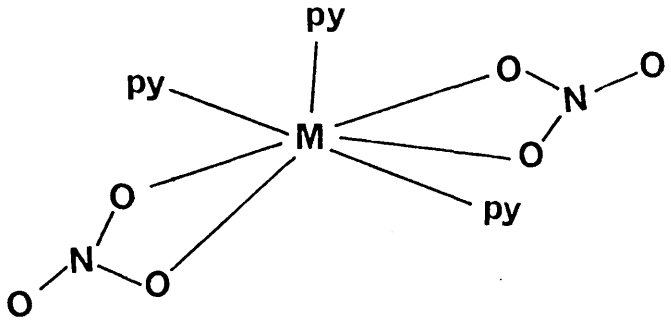


FIGURE II.20

Some suggested structures for $M(py)_3(NO_3)_2$

D 7-Coordinate



E Ionic Species

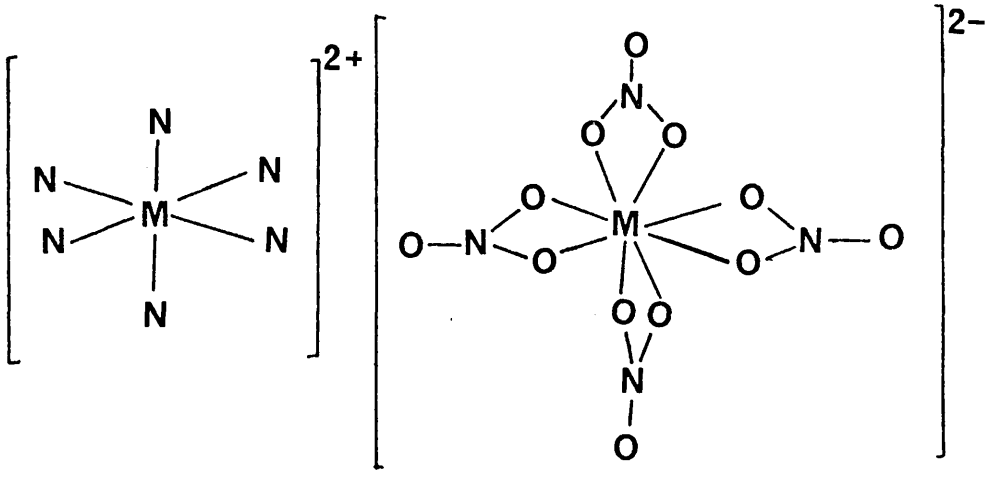


FIGURE II.20 (cont)

II.2.3 CRYSTAL AND MOLECULAR STRUCTURES OF THE COMPLEXES $M(py)_3(NO_3)_2$ (M = Co(II), Cu(II), Zn(II))

II. 2. 2. CRYSTAL AND MOLECULAR STRUCTURES OF THE COMPLEXES $M(py)_3(NO_3)_2$ (M = Co(II), Cu(II), Zn(II))

(a) Materials Used in the Determinations

Preparative details previously described in the literature [141, 170, 176, 179] produced satisfactory crystals for the X-ray analyses.

(b) Experimental and Results

Full experimental details, atomic parameters, thermal parameters and structure-factor tables are given in Appendix IV.

Figures II. 21 and II. 22 show the atomic numbering scheme and the molecular packing respectively for the three complexes. Table II. VIII lists interatomic dimensions and Table II. IX gives some least-squares best planes calculated through the molecules.

(c) Discussion

The three analyses have revealed that the complexes possess monomeric structures in which all the pyridine and nitrate groups are coordinated to the central metal atom in accordance with the predictions on the infrared and conductivity measurements [141, 145, 170, 176, 179]. However the crystallographic requirement that the molecules possess two-fold symmetry (the metal atom and atoms N(3) and C(8) of one of the

pyridine moieties lie on the symmetry axis), precludes all of the predicted structures (II. 2. 1) which possessed non-equivalent nitrato-coordination.

The overall molecular geometries of the three complexes show slight but marked differences, particularly in the detailed nitrato-coordination. In all three cases, the nitrate groups are asymmetrically orientated to the metal atom with the degree of asymmetry increasing in the order Co(II)<Zn(II)<Cu(II). For the cobalt and zinc complexes, the bonding is unequivocally bidentate whereas, for the copper complex the asymmetry of the copper-nitrate coordination is so great that the nitrato-groups are on the borderline between bidentate and unidentate coordination.

The shortest metal-ligand distances in the cobalt and zinc complexes are significantly longer than those normally found in corresponding Co(II) and Zn(II) 4, 5, and six-coordinate complexes [184]. This lengthening of bond lengths by ca. 0.1 Å has also been found for the $M(NO_3)_4^{2-}$ ion (M = Co(II), Mn(II) and Zn(II) [52, 73]. In the latter series of complexes, the asymmetric bidentate coordination of the nitrate groups apparently provides the most favourable steric arrangement of four nitrate moieties around a small central metal ion to produce eight-coordinate species. Since the steric requirements of seven-coordinate complexes cannot be much less, particularly when three positions are occupied by bulky pyridine groups, the asymmetry of the nitrato-coordination and the lengthening of other metal-ligand bonds is not unexpected.

For $Cu(py)_3(NO_3)_2$, the nitrate groups are much more asymmetric, which relieves the steric requirements at the copper atom and enables the pyridine functions to be relatively more closely bound.

The difference in M-O distances is significant [$\overline{M\text{-}O(2)} - \overline{M\text{-}O(1)}$ = 0.104 Å (Co), 0.186 Å (Zn), 0.560 A (Cu)] and the trend in individual metal-oxygen bond lengths is reflected in those frequencies assigned to ν(M-O) in the far infrared spectra [141, 145, 170]. For the cobalt and zinc complexes, the bond lengths are in Irving-Williams order but, for the copper compound, the situation is apparently more complicated than the series would predict.

For the cobalt and zinc complexes, the formal arrangement around the metal atom is seven-coordinate in a structure which may be related to a five-coordinate, square-based, pyramidal geometry using the line of centre approach of Cotton et al [64, 73], where the nitrate groups are considered to occupy single coordination sites. Alternatively, the seven-coordinate geometry may be described as a distorted pentagonal bipyramid but, using this description, it is difficult to account for the long Cu-0 distances Cu-0(2), Cu0'(2) found in $Cu(py)_3(NO_3)_2$.

Yet another interpretation of the stereochemistry may be achieved by considering the completion of a distorted octahedral coordination using as the sixth donor position, a line bisecting the M-O(1) and M-0'(1) bonds. This approach becomes relatively more important when the distortion of the copper complex is considered, and has already been invoked in descriptions of the

molecular geometries of the other copper complexes, $[Cu(py)_2(NO_3)_2]_2 \cdot py$ [75, 76] (Figure II.6, $Cu(NO_3)_2 \cdot 2.5H_2O$ [44] (Figure II.9) and $Cu(\alpha\text{-pic})_2(NO_3)_2$ [77-9] (Figures III.5 and III.6). In the latter complexes, the copper atom is surrounded by four short-bonded atoms in a square-planar arrangement. Below the plane are the two longer-bonded oxygens of the nitrate groups and above is an atom in a long-bond position although, for $Cu(\alpha\text{-pic})_2(NO_3)_2$, this latter position is blocked by the cis α-methyl groups. If this configuration were adopted in $Cu(py)_3(NO_3)_2$, one of the pyridine groups would be required to occupy the long-bond position above the square-plane. Since the Cu(II) ion is known to prefer to coordinate to nitrogen rather than to oxygen [185], a more favourable situation therefore prevails if the long-bond positions are occupied by oxygens from the nitrate groups. Thus, in the present copper complex, the pyridine groups occupy three corners of a square-plane whilst the fourth corner extends midway between the two shortest-bonded oxygens. This allows the long-bonded oxygens of the nitrato groups to occupy the axial position to this plane, (Figure II.23), so that effectively, by comparison with the cobalt and zinc complexes, a distortion of the type predicted by the Jahn-Teller effect is observed.

The Jahn-Teller theorem accounts for distortions in complexes with six equivalent ligands which give degenerate ground states. However, in Cu(II) complexes containing non-equivalent ligands, the environment around the copper may be considered effectively as a regular octahedral field [186] if the distances of the

inequivalent ligands are so arranged that higher positions in the spectrochemical series are exactly counterbalanced by longer bonds. A distortion is then required to remove this 'effective' regular octahedral symmetry.

The presence of the static Jahn-Teller effect [187] is therefore clearly demonstrated in the present series of complexes. The formal ionic radius of Cu(II) falls between the radii of Co(II) and Zn(II), and moreover, the individual steric bulk of each ligand does not alter from complex to complex throughout this series. Since all three complexes adopt the same crystal packing, the molecular geometry of $Cu(py)_3(NO_3)_2$ might be expected to be intermediate between those of Co(II) and Zn(II). As this is not so, the sole remaining factor to be accounted for is the nature of the bonding in the copper complex compared to that in the other two. If the overall symmetry of these complexes is considered as effectively C_{2v}, the Cu(II) ion will have an orbitally degenerate ground state and thus the field will be distorted to remove this degeneracy.

The only structure of a tris-pyridine complex previously reported is that of $Cu(py)_3(CH_3CO_2)_2$ [188]. However, in this complex only two of the pyridines are coordinated and the molecular geometry bears a closer relationship to the stereochemistry in $Cu(pyrazine)(NO_3)_2$ [46] than that found in the present series of compounds.

For $Co(py)_3(NO_3)_2$, a slight polarisation effect is observed in the nitrate groups, with the N-O bond adjacent to the

strongest metal-oxygen interaction N-O(1) longer than the terminal N-O bond [N-O(3)]. In the corresponding bonds for the zinc and copper complexes, the same trend is observed although, in these cases, the differences are not statistically significant. The O-N-O bond angles all show distortions from the trigonal value of 120^{o}, such that the largest angle is opposite the strongest M-O interaction in each case. The degree of bidentate character of the nitrate groups is reflected in the M-O(1)-N(2) angles (M-O(1)-N(2) = $98.0(7)^{o}$ (Co), $101.0(9)^{o}$ (Zn), $109.9(6)^{o}$ (Cu)) which in the copper complex approaches the angle expected for unidentate coordination of 110^{o} (106).

In the molecular structures, all of the groups are arranged so as to minimise steric interactions. Intermolecular contacts are all equal to or greater than the sums of the relevant van der Waals radii.

TABLE II.VIII

$M(py)_3(NO_3)_2$ (M = Co^{II}, Cu^{II}, Zn^{II})

Interatomic distances (Å) and angles (°) with estimated standard deviations in parentheses

	Zn	Co	Cu
M-O(1)	2.232(13)	2.207(9)	2.154(7)
M-O(2)	2.418(12)	2.311(9)	2.732(9)
M-N(1)	2.129(10)	2.152(9)	2.018(8)
M-N(3)	2.201(12)	2.124(11)	2.064(9)
N(1)-C(1)	1.35(2)	1.340(15)	1.336(11)
N(1)-C(5)	1.39(2)	1.380(20)	1.350(12)
C(1)-C(2)	1.36(2)	1.331(20)	1.385(13)
C(2)-C(3)	1.41(2)	1.398(21)	1.396(16)
C(3)-C(4)	1.37(2)	1.362(21)	1.348(18)
C(4)-C(5)	1.36(2)	1.403(20)	1.376(15)
N(3)-C(6)	1.32(2)	1.338(13)	1.362(10)
C(6)-C(7)	1.37(2)	1.378(16)	1.428(12)
C(7)-C(8)	1.40(2)	1.403(15)	1.360(12)
N(2)-O(1)	1.26(2)	1.287(13)	1.261(10)
N(2)-O(2)	1.24(2)	1.235(13)	1.248(13)
N(2)-O(3)	1.21(2)	1.223(13)	1.232(12)

TABLE II.VIII (cont)

(b) Interbond angles

	Zn	Co	Cu
O(1)-M-O(2)	53.0(4)	55.8(3)	50.0(3)
O(1)-M-O'(1)	87.2(3)	82.4(3)	91.4(3)
O(1)-M-O'(2)	140.2(3)	137.9(3)	141.3(3)
O(1)-M-N(1)	88.6(3)	91.3(3)	92.0(3)
O(1)-M-N'(1)	83.7(3)	83.7(3)	85.2(2)
O(1)-M-N(3)	136.4(3)	138.8(2)	134.3(2)
O(2)-M-O'(2)	166.8(3)	166.3(3)	168.8(3)
O(2)-M-N(1)	92.4(3)	91.7(4)	92.5(3)
O(2)-M-N'(1)	88.4(4)	89.1(3)	87.9(3)
O(2)-M-N(3)	83.4(3)	83.2(2)	84.4(2)
N(1)-M-N'(1)	169.4(4)	173.3(4)	176.0(3)
N(1)-M-N(3)	95.3(3)	93.4(2)	92.0(2)
C(2)-C(1)-N(1)	124.0(13)	122.9(12)	123.1(9)
C(1)-C(2)-C(3)	119.3(15)	118.5(13)	118.4(10)
C(2)-C(3)-C(4)	116.9(15)	119.9(14)	118.4(10)
C(3)-C(4)-C(5)	122.5(16)	117.1(13)	120.8(11)
C(4)-C(5)-N(1)	120.5(15)	124.3(12)	121.8(10)
M-N(1)-C(1)	123.4(9)	121.6(8)	121.0(6)
M-N(1)-C(5)	119.9(9)	121.1(8)	121.3(6)
C(1)-N(1)-C(5)	116.7(12)	117.1(10)	117.6(8)
C(7)-C(6)-N(3)	120.9(13)	121.8(11)	119.1(8)
C(6)-C(7)-C(8)	119.3(14)	119.3(12)	118.5(10)
C(7)-C(8)-C'(7)	116.4(14)	117.9(12)	122.7(11)
M-N(3)-C(6)	118.5(8)	120.0(6)	119.1(5)
C(6)-N(3)-C'(6)	123.0(13)	120.0(11)	121.9(11)
M-O(1)-N(2)	101.0(9)	98.0(7)	109.9(6)
M-O(2)-N(2)	92.6(8)	91.6(6)	82.3(6)
O(1)-N(2)-O(2)	112.6(11)	114.0(9)	117.2(8)
O(1)-N(2)-O(3)	121.4(14)	121.0(10)	119.7(9)
O(2)-N(2)-O(3)	126.0(12)	125.0(11)	123.0(9)

TABLE II.VIII (cont)

(c) Intramolecular contacts

	Zn	Co	Cu
M. . .C(1)	3.09	3.07	2.94
M. . .C(5)	3.07	3.06	2.95
M. . .C(6)	3.03	3.02	2.97
M. . .N(2)	2.77	2.68	2.84
O(1). . .C(1)	3.49	3.42	3.45
O(1). . .C'(1)	3.03	3.10	2.96
O(1). . .O'(1)	3.08	2.91	3.08
O(1). . .O(2)	2.08	2.12	2.13
O(1). . .O(3)	2.16	2.18	2.17
O(1). . .N(1)	2.91	2.91	2.83
O(1). . .N'(1)	3.05	3.12	3.00
O(2). . .C(5)	3.30	3.27	3.29
O(2). . .C'(6)	3.05	2.98	3.09
O(2). . .O(3)	2.18	2.18	2.18
O(2). . .N(1)	3.18	3.13	3.33
O(2). . .N'(1)	3.29	3.20	3.47
O(2). . .N(3)	3.08	2.95	3.26

TABLE II.VIII (cont)

(d) Intermolecular contacts

	Zn	Co	Cu
O(1). . .C(3)^{I}	3.49	3.45	3.47
O(1). . .C(8)^{II}	3.25	3.23	3.28
O(2). . .C(7)^{III}	3.57	3.59	3.48
O(3). . .C(2)^{I}	3.53	3.52	3.47
O(3). . .C(3)^{I}	3.55	3.57	3.49
O(3). . .C(4)^{IV}	3.46	3.44	3.34
O(3). . .C(4)^{III}	3.48	3.48	3.52
O(3). . .C(5)^{IV}	3.49	3.55	3.52
O(3). . .C(5)^{III}	3.59	3.63	3.63
O(3). . .C(6)^{III}	3.43	3.44	3.41
O(3). . .C(7)^{IV}	3.52	3.49	3.63
N(2). . .C(7)^{III}	3.54	3.58	3.59

Roman numerals as superscripts refer to the following equivalent positions with respect to the reference molecule at x, y, z.

I	1 - x, 1 - y, -z
II	x, -1 + y, z
III	-1/2 + x, -1/2 + y, z
IV	1/2 - x, 3/2 - y, -z

TABLE II.IX

$M(py)_3(NO_3)_2$ (M = Co^{II}, Cu^{II}, Zn^{II})

Least-squares best planes through the molecules. The equations are in the form $kX' + \ell Y' + mZ' = n$, where X', Y' and Z' are coordinates in Å. Distances of atoms from planes (Å) are given in square brackets.

	k	ℓ	m	n
Plane(1): O(1)-(3), N(2)				
(i) Zn	0.4344	0.0901	-0.8962	1.0476
O(1) -0.003, O(2) -0.003, O(3) -0.003, N(2) 0.009, Zn 0.325				
(ii) Co	0.4115	0.1149	-0.9041	1.1419
O(1) -0.002, O(2) -0.002, O(3) -0.002, N(2) 0.006, Co 0.267				
(iii) Cu	0.3992	0.1077	-0.9105	1.0288
O(1) -0.005, O(2) -0.005, O(3) -0.005, N(2) 0.014, Cu 0.263				
Plane(2): C(1)-(5), N(1)				
(i) Zn	-0.7875	0.5890	-0.1816	-1.2019
C(1) -0.003, C(2) -0.022, C(3) 0.029, C(4) -0.010, C(5) -0.015, N(1) 0.022, Zn 0.062				
(ii) Co	-0.7827	0.5965	-0.1777	-1.0632
C(1) -0.018, C(2) -0.006, C(3) 0.018, C(4) -0.006, C(5) -0.018, N(1) 0.030, Co 0.020				
(iii) Cu	-0.7429	0.6533	-0.1461	-0.5517
C(1) -0.001, C(2) -0.002, C(3) -0.003, C(4) 0.013, C(5) -0.016, N(1) 0.010, Cu 0.047				

TABLE II.IX (cont)

	k	ℓ	m	n
Plane(3): C(6)-(8), N(3)				
(i) Zn	-0.3536	-0.0071	-0.9354	-4.0768
C(6) -0.020, C(7) 0.019, C(8) -0.009, N(3) 0.010, Zn 0.026				
(ii) Co	-0.3910	-0.0010	-0.9204	-4.1552
C(6) -0.003, C(7) 0.003, C(8) -0.001, N(3) 0.002, Co 0.004				
(iii) Cu	-0.2995	-0.0041	-0.9541	-3.7670
C(6) -0.011, C(7) 0.011, C(8) 0.006, N(3) -0.006, Cu 0.014				

Dihedral angles (^{o}) between planes

	Zn	Co	Cu
Plane (1)-(2)	82.8	84.7	84.7
Plane (1)-(3)	46.8	47.8	41.5
Plane (2)-(3)	63.6	62.0	68.9

FIGURE II.21

$M(py)_3(NO_3)_2$ ($M = Co^{II}$, Cu^{II}, Zn^{II})

A view of the molecule along b showing the atomic numbering

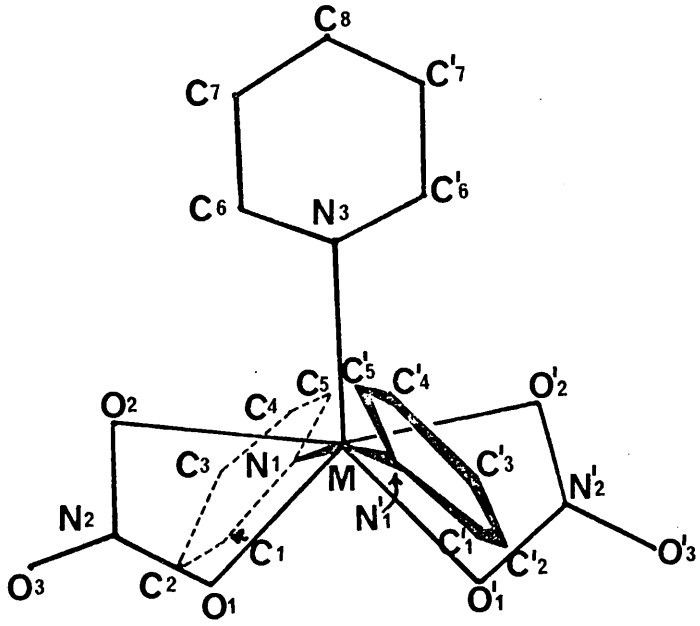
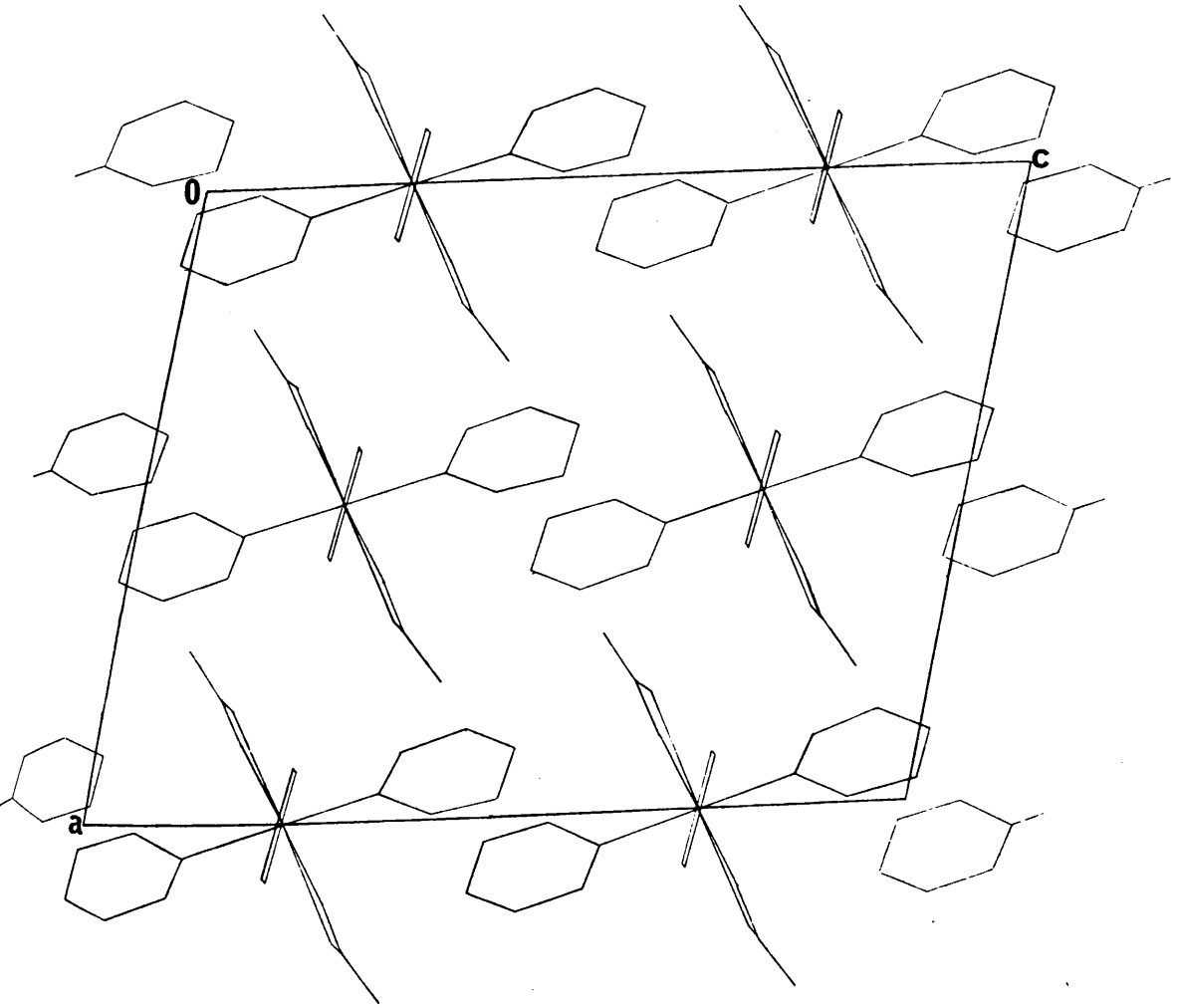

C8
C7
C'7
C6
N3
C'6
C'5
C5
C'4
O'2
O2
C4
C3
N1
M
C'3
N'2
N2
N'1
C1
C'1
C'2
O'3
O3
C2
O1
O'1

FIGURE II.22

$M(py)_3(NO_3)_2$ ($M = Co^{II}$, Cu^{II}, Zn^{II})

The molecular packing viewed along the b axis


0
c
a

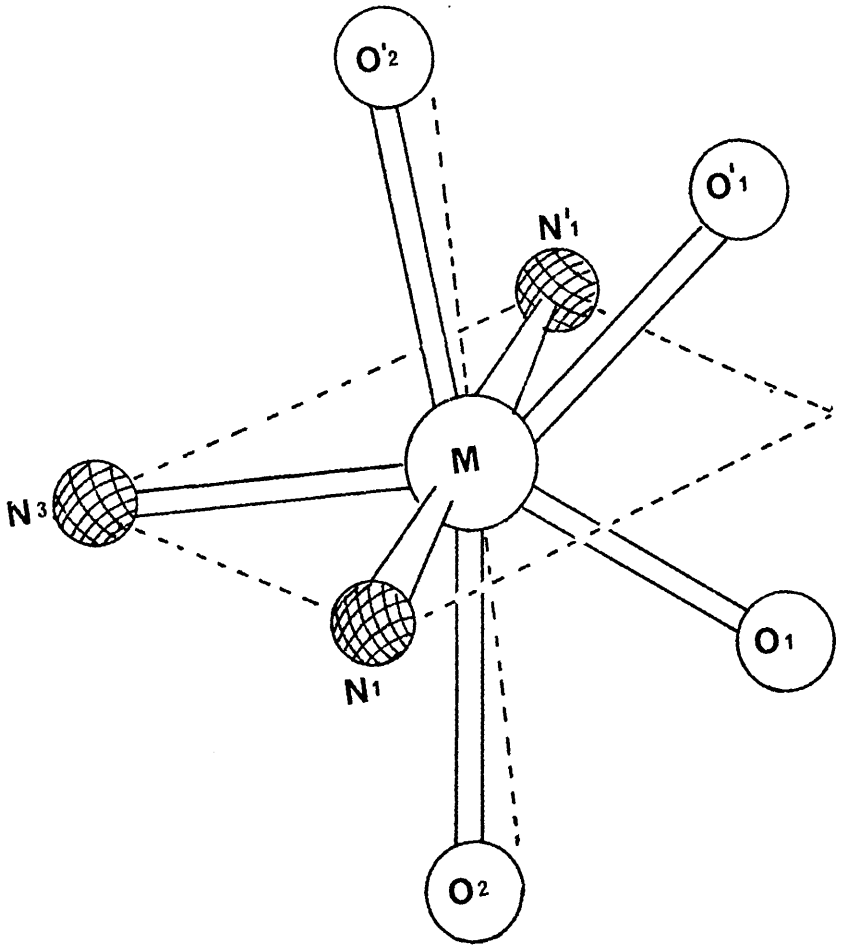


FIGURE II.23

II.2.3 CRYSTAL AND MOLECULAR STRUCTURE OF DINITRATOTRIS(PYRIDINE)-CADMIUM(II)

II. 2. 3. CRYSTAL AND MOLECULAR STRUCTURE OF DINITRATOTRIS(PYRIDINE)-CADMIUM(II), $Cd(py)_3(NO_3)_2$

(a) Material Used in the Determination

The preparation previously described in the literature [170] produced satisfactory crystals for the X-ray analysis.

(b) Experimental and Results

Full experimental details, atomic parameters, thermal parameters and structure-factor tables are given in Appendix V.

Figures II. 24 and II. 25 show the atomic numbering scheme and the molecular packing respectively. Table II. X lists interatomic dimensions and Table II. XI gives some least-squares best planes calculated through the molecule.

(c) Discussion

The analysis has revealed that $Cd(py)_3(NO_3)_2$ is monomeric in direct contrast to the predicted polymeric nature of the complex [170] and that the cadmium atom is surrounded by three pyridine and two bidentate nitrate groups (Figure II. 24). The crystallographic requirement for two-fold molecular symmetry found for the three complexes $M(py)_3(NO_3)_2$ (II. 2. 2) (M = Co(II),

Cu(II), Zn(II) [80, 81]), is maintained in the present case and in this sense the molecular packing of all four compounds are similar. However, $Cd(py)_3(NO_3)_2$ is distinguished from the other three complexes by positioning of the molecules in the y-direction of the crystal, and also in the spatial arrangement of the ligands about the two-fold axis, there being no obvious, nor direct, relationship between the coordinates of atoms in the present complex and those of the other complexes. Comparison of intermolecular distances in all four complexes does not indicate any striking changes in the efficiency of packing as a result of these differences, and indeed many of the contacts do not vary greatly. In each case, the closest approaches between molecules are either equal to or greater than the sums of the corresponding van der Waals radii.

The largest contrast between the molecular structure of $Cd(py)_3(NO_3)_2$ and the molecular structures of the other tris-pyridine complexes, lies in the mode of nitrate coordination. In the present complex, the cadmium-oxygen distances (Cd-O(1) 2.444(9) Å, Cd-O(2) 2.491(10) Å), although just significantly different, indicate that the nitrate groups are almost symmetrically coordinated, whereas the corresponding dimensions in the Co(II), Cu(II) and Zn(II) complexes indicate distinct if differing degrees of asymmetry in the metal-nitrate bonding. Considering the differences in respective metal-oxygen distances in each of the Cd(II), Co(II) and Zn(II) complexes as indicating the individual asymmetries of nitrate coordination, shows that these three complexes form a

well-defined series $(\overline{M\text{-}O(2)} - \overline{M\text{-}O(1)}) = 0.047$ Å (Cd), 0.104 Å (Co), 0.186 Å (Zn) in which the asymmetry shows an expected increase with decreasing metal ionic radius. Thus, the larger size of the cadmium can more readily accommodate a regular seven-coordinate environment. The Cu(II) complex is an anomalous member of the series as a result of static Jahn-Teller distortions [81] (II. 2. 2).

Comparison of the structures of $Zn(py)_2(NO_3)_2$ [96] and $Zn(py)_3(NO_3)_2$ [80, 81] with the present complex also demonstrates this size effect. There are no ligand field stabilisation effects in the Zn(II) and Cd(II) ions because of their completed d shells and the stereochemistry of their complexes is determined solely by considerations of size, electrostatic forces and covalent bonding forces [189]. Thus, Zn(II) has a tendency to assume a coordination number of four whereas Cd(II) is more likely to be six-coordinate. Examples of corresponding complexes of Zn(II) and Cd(II) showing these preferences are given in Table II. XII. The decreasing asymmetry of the nitrate coordination in the series $Zn(py)_2(NO_3)_2$ $Zn(py)_3(NO_3)_2$ $Cd(py)_3(NO_3)_2$ is also in agreement with the expansion of coordination from Zn(II) to Cd(II).

Although the cadmium-ligand bonds in the present complex are long compared with previously recorded values for six-coordinate cadmium complexes [197], the Cd-O distances are of the same order as found in the eight-coordinate $Cd(NO_3)_2 \cdot 4H_2O$ [44a] (Cd-O(nitrate) = 2.44 and 2.59 Å). A similar effect was noted in

the structures of the other tris-pyridine complexes [80, 81] (II. 2. 2).

If the nitrate groups are regarded as occupying single coordination sites [64, 73], the structure may be described on the basis of distorted square-based pyramidal geometry. Alternatively, the seven-coordinate geometry may be rationalised by regarding the pyridines as occupying three corners of a square-plane with the fourth corner bisecting two of the oxygens of the nitrate groups M-O(1) and M-O'(1). The remaining two oxygens [O(2) and O'(2)] then occupy the sites axial to this plane (Figure II. 23). This type of description of the bonding has been used in explaining the distortion present in the complex $Cu(py)_3(NO_3)_2$ [81] (II. 2. 2).

A further description of the molecular structure is to consider the atoms surrounding the cadmium as forming a distorted pentagonal bipyramid (Figure II. 26). The nitrogen atoms N(1) and N'(1) are in the axial positions while the equatorial plane is occupied by four oxygen atoms from the nitrate groups [O(1), O(2), O'(2) and O'(1)] and the nitrogen atom of the remaining pyridine [N(3)]. The inequivalent Cd-O and Cd-N distances reflect the positions of the ligands in the spectrochemical series [198] and the distortions in the interatomic angles at the cadmium atom in the equatorial plane from the ideal value of 72° arise because the oxygen atoms of the nitrate groups [O(1), O(2) and O'(1), O'(2)] cannot accommodate such a large angle. The N(1)-Cd-N(3) = N'(1)-Cd-N(3) angle ($97.1(2)^{\circ}$) is increased from 90° by steric repulsion between the pyridine groups.

Very few seven-coordinate cadmium complexes are known. $Cd_2Zn(PO_4)_2$ has been reported to contain three distinctly different cadmium coordination-geometries [199]. One of these is seven-coordinate cadmium in a distorted pentagonal bipyramidal arrangement. The distortion produces Cd-O distances in the range 2.26-2.67(2) Å and can be related to the chelating character of the ligands. Seven-coordinate cadmium has also been postulated in the crystal structure of $Cd_2P_2O_7$ but no description of the coordination polyhedron was given [200].

Another more recent example of seven-coordination is in $Cd(CH_3CO_2)_2(H_2O)_2$ where the molecular geometry has been described as distorted square base-trigonal cap, and the Cd-O distances are in the range 2.292-2.597(4) Å [148]. The distortions in this complex probably result from hydrogen bonding and from the bridging/chelating nature of the acetate groups.

In the present complex, there is a polarisation effect discernable in the nitrate groups with the terminal N-O bond (1.213(19) Å) shorter than the other two (1.263(14), 1.261(14) Å). The O-N-O angles are all distorted from 120° and the Cd-O-N angles (Cd-O(1)-N(2) = 97.4(6)°, Cd-O(2)-N(2) = 95.1(7)°) approach the values normally found for symmetrical bidentate metal-nitrato bonding [36]. As for previous members of the series [80, 81] (II. 2. 2), all the metal-bonded groups are arranged so as to minimise steric interaction.

TABLE II.X

$Cd(py)_3(NO_3)_2$

Interatomic distances (Å) and angles (°) with estimated standard deviations in parentheses

(a) Bonded distances

Cd-O(1)	2.444(9)	C(3)-C(4)	1.393(21)
Cd-O(2)	2.491(10)	C(4)-C(5)	1.392(18)
Cd-N(1)	2.301(9)	N(3)-C(6)	1.330(15)
Cd-N(3)	2.347(14)	C(6)-C(7)	1.402(18)
N(1)-C(1)	1.365(18)	C(7)-C(8)	1.325(16)
N(1)-C(5)	1.335(15)	N(2)-O(1)	1.263(14)
C(1)-C(2)	1.363(23)	N(2)-O(2)	1.261(14)
C(2)-C(3)	1.374(22)	N(2)-O(3)	1.213(19)

TABLE II.X (cont)

(b) Interbond angles

O(1)-Cd-O(2)	51.3(3)	C(3)-C(4)-C(5)	116.2(12)
O(1)-Cd-O'(1)	92.8(3)	C(4)-C(5)-N(1)	123.9(12)
O(1)-Cd-O'(2)	143.9(2)	Cd-N(1)-C(1)	120.7(8)
O(1)-Cd-N(1)	86.2(3)	Cd-N(1)-C(5)	121.8(8)
O(1)-Cd-N'(1)	84.1(3)	C(1)-N(1)-C(5)	117.6(11)
O(1)-Cd-N(3)	133.6(2)	C(7)-C(6)-N(3)	120.4(8)
O(2)-Cd-O'(2)	164.8(3)	C(6)-C(7)-C(8)	120.1(13)
O(2)-Cd-N(1)	95.9(3)	C(7)-C(8)-C'(7)	119.8(12)
O(2)-Cd-N'(1)	86.9(2)	Cd-N(3)-C(6)	120.4(8)
O(2)-Cd-N(3)	82.4(2)	C(6)-N(3)-C'(6)	119.2(11)
N(1)-Cd-N'(1)	165.8(3)	Cd-O(1)-N(2)	97.4(6)
N(1)-Cd-N(3)	97.1(2)	Cd-O(2)-N(2)	95.1(7)
C(2)-C(1)-N(1)	122.8(13)	O(1)-N(2)-O(2)	115.5(11)
C(1)-C(2)-C(3)	118.3(15)	O(1)-N(2)-O(3)	122.6(11)
C(2)-C(3)-C(4)	121.3(14)	O(2)-N(2)-O(3)	121.9(12)

TABLE II.X (cont)

(c) Intramolecular distances

Cd. . .C(1)	3.22	O(1). . .N(1)	3.24
Cd. . .C(5)	3.21	O(1). . .N'(1)	3.18
Cd. . .C(6)	3.23	O(2). . .C'(1)	3.50
Cd. . .N(2)	2.89	O(2). . .C(6)	3.14
O(1). . .C(5)	3.16	O(2). . .O(3)	2.16
O(1). . .O'(1)	3.54	O(2). . .N(1)	3.54
O(1). . .O(2)	2.14	O(2). . .N'(1)	3.30
O(1). . .O(3)	2.17	O(2). . .N(3)	3.19

TABLE II.X (cont)

(d) Intermolecular contacts

O(1). . .C(3)^{I}	3.42	O(3). . .C(2)^{IV}	3.40
O(1). . .C(7)^{II}	3.52	O(3). . .C(2)^{V}	3.51
O(1). . .C(8)^{II}	3.24	O(3). . .C(4)^{I}	3.55
O(2). . .C(4)^{III}	3.58	O(3). . .C(6)^{V}	3.44
O(3). . .C(1)^{IV}	3.43	O(3). . .C(7)^{V}	3.56
O(3). . .C(1)^{V}	3.47	N(2). . .C(7)^{V}	3.55

Roman numerals as superscripts refer to the following equivalent positions with respect to the reference molecule at x, y, z.

I	1/2 + x, 3/2 - y, 1/2 + z
II	x, 1 + y, z
III	1/2 - x, -1/2 + y, 1/2 - z
IV	x, 1 - y, 1/2 + z
V	1/2 - x, 1/2 + y, 1/2 - z

TABLE II.XI

$Cd(py)_3(NO_3)_2$

Least-squares best planes through the molecule. The equations are in the form $kX' + \ell Y' + mZ' = n$, where X', Y' and Z' are coordinates in Å. Distances of atoms from planes (Å) are given in square brackets

	k	ℓ	m	n
Plane(1):				
O(1)-(3), N(2)	-0.9431	0.0013	-0.3325	-5.5546
O(1) 0.004, O(2) 0.004, O(3) 0.005, N(2) -0.013, Cd -0.292				
Plane(2):				
C(1)-(5), N(1)	0.4810	0.4914	-0.7260	4.0159
C(1) -0.004, C(2) 0.008, C(3) -0.004, C(4) 0.007, C(5) 0.009, N(1) -0.005, Cd -0.005				
Plane(3):				
C(6)-(8), N(3)	-0.5270	-0.0014	-0.8498	-4.3869
C(6) 0.004, C(7) -0.004, C(8) 0.002, N(3) -0.002, Cd -0.005				

Dihedral angles between planes (°)

Plane (1)-(2)	78
Plane (1)-(3)	39
Plane (2)-(3)	69

TETRAHEDRAL	POLYMERIC OCTAHEDRAL
$Zn(NH_3)_2Br_2$ [190]	$Cd(NH_3)_2Br_2$ [193]
$Zn(NH_3)_2Cl_2$ [191]	$Cd(NH_3)_2Cl_2$ [194]
$Zn(py)_2Cl_2$ [192]	$Cd(py)_2Cl_2$ [195]
$Zn(py)_2(N_3)_2$ [172]	$Cd(py)_2(N_3)_2$ [196]

TABLE II.XII

A comparison of corresponding Zinc and Cadmium Complexes

FIGURE II.24

$Cd(py)_3(NO_3)_2$

A view of the molecule along b showing the atomic numbering

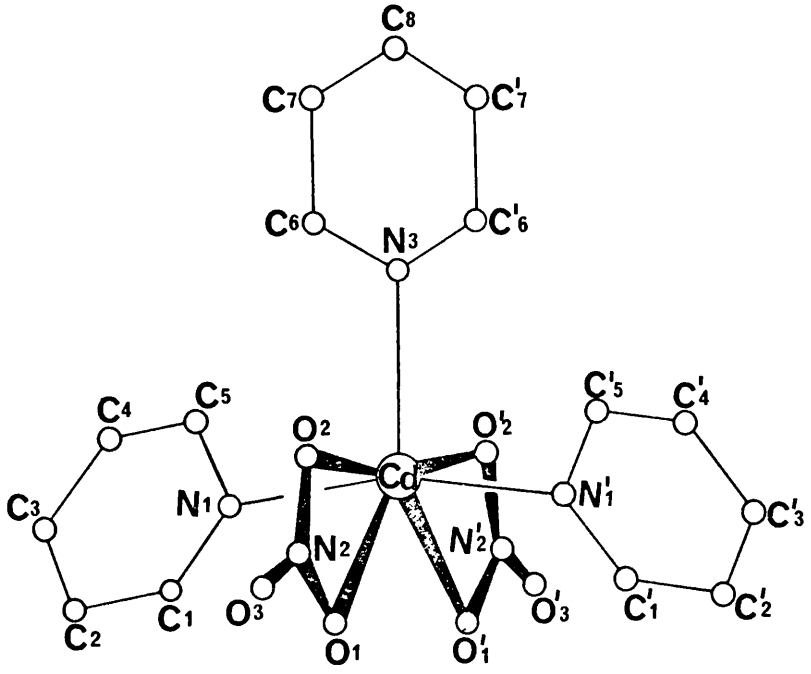
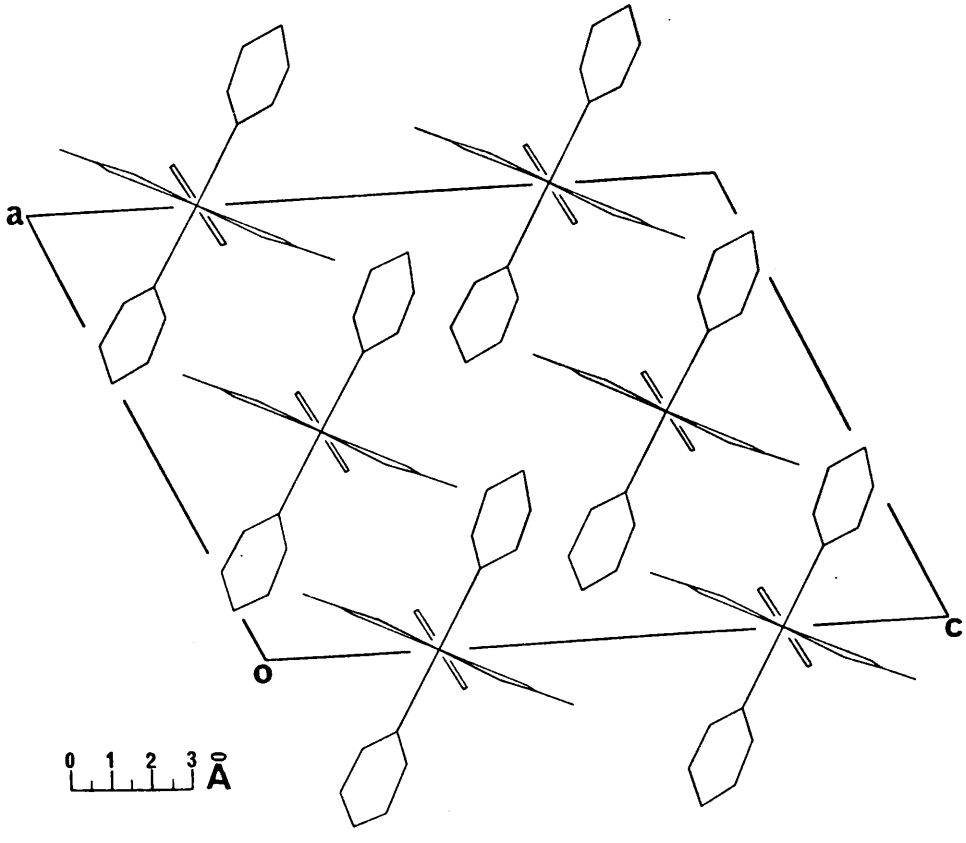

C8
C7
C'7
C6
N3
C'6
C4
C5
O2
O'2
C'5
C'4
C3
N1
Co
N'1
C'3
N2
N'2
O3
O'3
C'1
C'2
C2
C1
O1
O'1

FIGURE II.25

$Cd(py)_3(NO_3)_2$

The molecular packing viewed along the b axis


a
o
c
0 1 2 3 Å

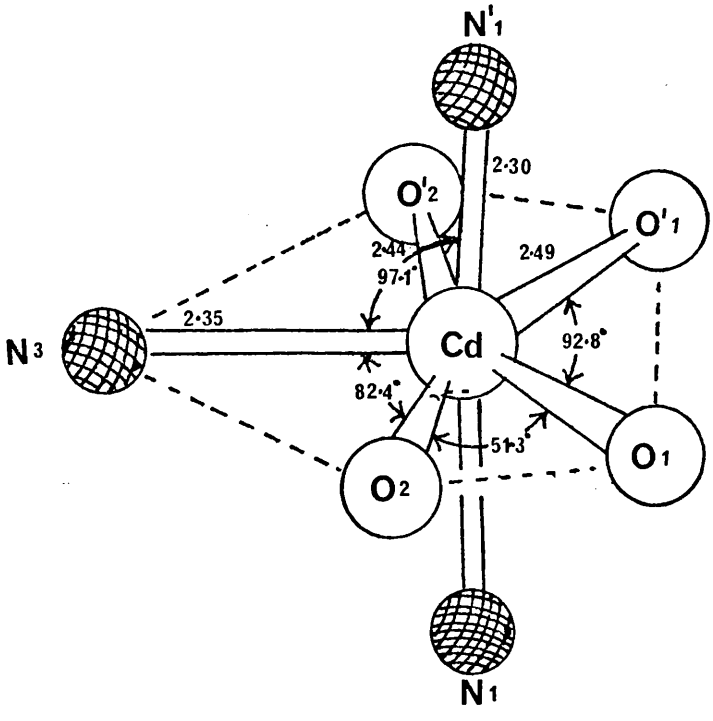


FIGURE II.26

The environment around Cd in $Cd(py)_3(NO_3)_2$

SECTION III

THE STRUCTURES OF SOME METAL-NITRATO COMPLEXES OF AMINES WITH GREATER STERIC REQUIREMENTS THAN PYRIDINE

CHAPTER 1

Dinitratobis(α-picoline)-copper(II)

CHAPTER 2

Aquo(dinitratobisquinoline)-cadmium(II)

CHAPTER 1

Dinitratobis(∝-picoline)-copper(II)

III.1.1. THE COPPER NITRATE-∝-PICOLINE SYSTEM

Several complexes of the type $L_2M(NO_3)_2$ (L = amine, M = Co(II), Ni(II), Cu(II) and Zn(II)), have been predicted to have structural features similar to those of $(Me_3PO)_2Co(NO_3)_2$ [64, 201] (Figure I.3). However, the X-ray analyses of $Cu(py)_2(NO_3)_2$ (as $[Cu(py)_2(NO_3)_2]_2 \cdot py$ [75, 76] - Section II.1.2) and $Zn(py)_2(NO_3)_2$ [96] (Section II.1.4) have revealed structures that are quite unrelated to this species, the copper complex in particular being a centrosymmetric dimer with asymmetric and non-equivalent nitrato-groups. Therefore, an investigation of copper(II) nitrate complexes with ligands bulkier than pyridine has been carried out to determine, if possible, the most favourable stereochemistry, or sterochemistries, of complexes of the type $Cu(L)_2(NO_3)_2$, where L is a unidentate, neutral ligand.

∝-Picoline is a convenient choice of ligand since the structures of the corresponding halide complexes, $Cu(py)_2Cl_2$ and $Cu(\alpha\text{-pic})_2Cl_2$, are known. The molecular structure of $Cu(py)_2Cl_2$ [202] (Figure III.1) may be described as polymeric, tetragonally-distorted octahedral. The copper atom is surrounded by two chlorine atoms and nitrogen atoms from two pyridine groups in a <u>trans</u> square-planar arrangement. The six-coordination is

FIGURE III.1

Molecular structure of $Cu(py)_2Cl_2$ (202)

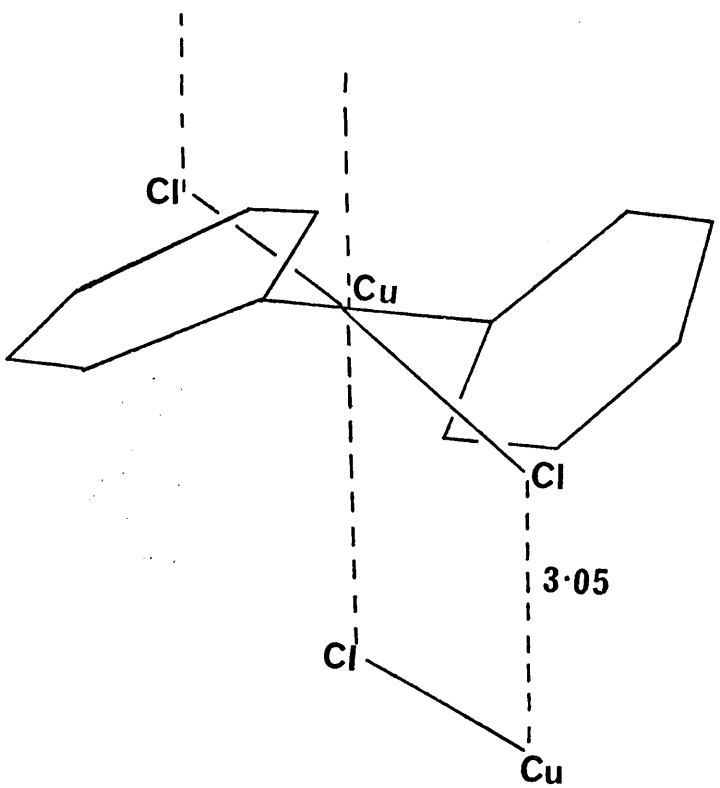
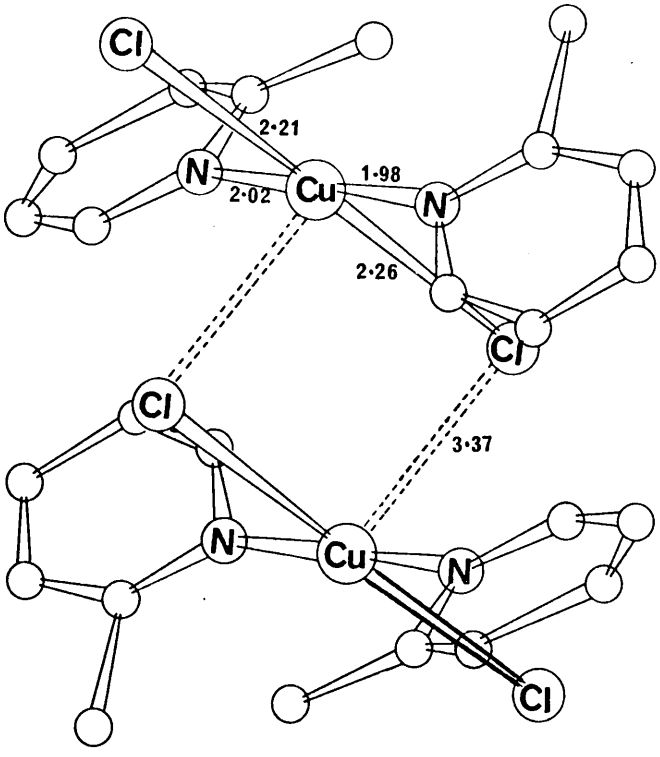


FIGURE III.2

The Molecular Structure of $Cu(\alpha\text{-pic})_2Cl_2$ (203)


Cl
2·21
N
2·02
Cu
1·98
N
2·26
Cl
Cl
3·37
N
Cu
N
Cl

completed by bridging chlorines above and below this plane. If the pyridine moieties are replaced by α-picoline groups, the latter are orientated so that the α-methyl groups lie in cis positions relative to each other. This effectively blocks one of the axial sites, thereby reducing the coordination of the copper to five and the molecular unit to a dimer [203] (Figure III. 2).

Since α-picoline complexes of Cu(II) are also known where the α-methyl groups are in trans positions [204, 205], prior to the X-ray investigation, two molecular structures for $Cu(\alpha\text{-pic})_2(NO_3)_2$ could be envisaged:

(i) with one axial site blocked (cis α-methyl groups);

(ii) with both axial sites blocked (trans α-methyl groups).

It was therefore important to ascertain which of these two configurations was formed and the effect of the configuration on the nitrate geometry and mode of bonding (particularly in comparison to the dimeric nature of $[Cu(py)_2(NO_3)_2]_2 \cdot py$.

Initially, we were aware of only one form of $Cu(\alpha\text{-pic})_2(NO_3)_2$ but Hathaway [206], in a single-crystal study of the e. s. r. and electronic spectra of this compound, obtained a second form. The existence of these two crystalline modifications represents an almost unique type of polymorphism, since both forms utilise the same space group symmetry with almost identical unit cells, yet have quite different crystal packing. To indicate the different natures of these two forms, Professor Hathaway has kindly sent the results of his single-crystal work (Figures III. 3 and

FIGURE III.5

The polarised single-crystal electronic spectra of $Cu(\alpha\text{-pic})_2(NO_3)_2$ - Form I

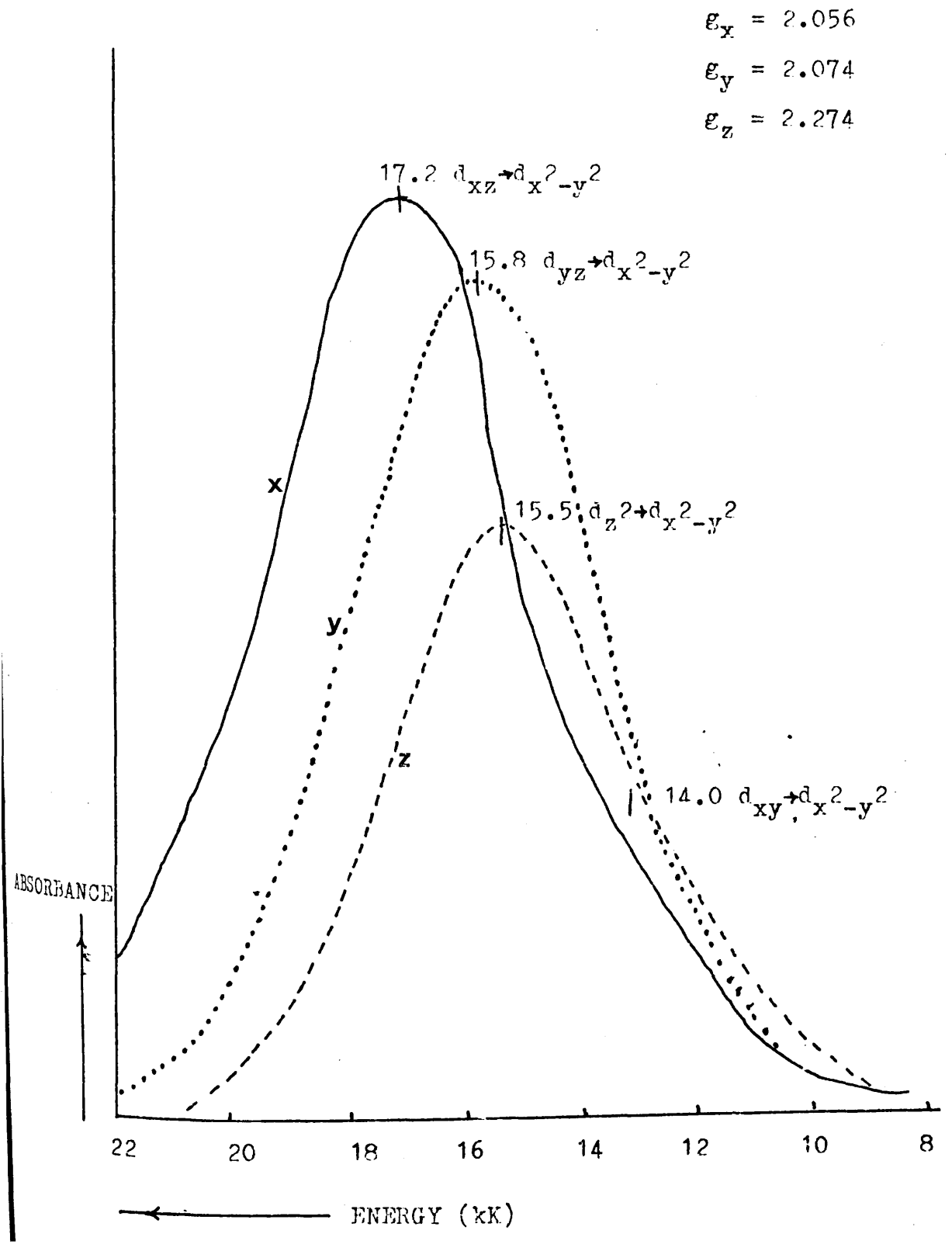
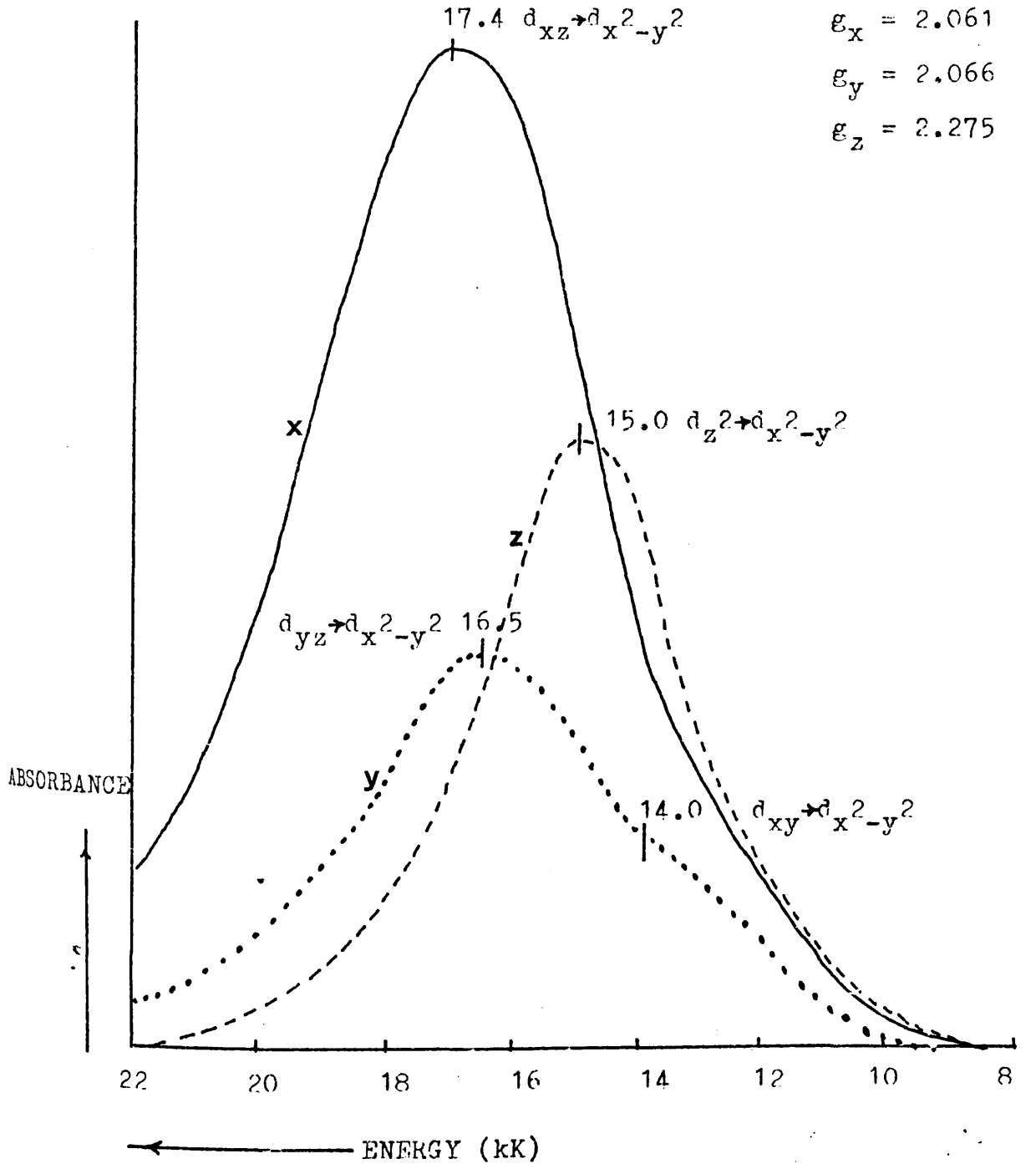


FIGURE III.4

The polarised single-crystal electronic spectra of $Cu(\alpha\text{-pic})_2(NO_3)_2$ - Form II



III. 4). These results have not been fully analysed at present but they are indicative of the slight differences in bonding resulting from the alignment of the molecules in the crystal for each case. Therefore, the structures of both modifications have been determined by three-dimensional X-ray diffraction techniques.

III.1.2. CRYSTAL AND MOLECULAR STRUCTURE OF TWO CRYSTALLINE FORMS OF DINITRATO-BIS(α-PICOLINE)-COPPER(II)

III. 1. 2. CRYSTAL AND MOLECULAR STRUCTURES OF TWO CRYSTALLINE FORMS OF DINITRATOBIS(∝-PICOLINE)-COPPER(II)

(a) Material Used in the Determination

Crystals were obtained according to the method of Lever [201]. The isolation of the two separate crystalline forms is dependent upon the temperature to which the crystallising liquid is heated before cooling (see Appendix VI).

(b) Experimental and Results

Full experimental details, atomic parameters, thermal parameters and structure-factor tables are given in Appendix VI.

Figures III. 5 and III. 6 show the atomic numbering schemes for forms I and II respectively. Figures III. 7 and III. 8 show the packing arrangements for the two forms. The interatomic dimensions from the determinations are listed in Table III. 1 while the results of some calculations of least-squares planes for portions of the molecular frameworks are given in Tables III. II (Form I) and III. III (Form II).

(c) Discussion

The two X-ray analyses reveal that both crystalline forms of $Cu(\alpha\text{-pic})_2(NO_3)_2$ contain very similar, but not identical,

molecular configurations which are based on a monomeric, six-coordinate structure in which the nitrate groups are asymmetrically bidentate with respect to the copper atom (Figures III. 5 and III. 6). One distinction between the two molecules is found in the respective non-equivalence and equivalence of the nitrate groups in Forms I and II. The non-equivalence of the nitrate groups in Form I (Cu-0(1) 2. 307(13), Cu-0(3) 2. 026(16), Cu-0(4) 1. 971(13) and Cu-0(6) 2. 557(7) Å) parallels the situation which exists in the dimeric molecule of $[Cu(py)_2(NO_3)_2]_2 \cdot py$ [75, 76] (II. 1. 2). This similarity is striking when the crystal packing of Form 1 is considered (Figure III. 7). It is apparent that centrosymmetrically-related molecules of this form are aligned throughout the crystal such that a relatively small reduction in intermolucular separation could produce dimerisation similar to that found in $[Cu(py)_2(NO_3)_2]_2 \cdot py$ were it not for the blocking action of the cis ∝-methyl groups. In Form II, the significant spatial relationship to the bis(pyridine) complex does not pertain, and the nitrate groups are not only equivalent (Cu-0(1) 2. 517(8), Cu-0(3) 1. 983(10), Cu-0(4) 2. 005(10) and Cu-0(6) 2. 551(7) Å), but show asymmetry of the same order as that found in $Cu(NO_3)_2 \cdot 2 \cdot 5H_2O$ [44] and in $Cu(C_2H_4N_2)(NO_3)_2$ [46].

It was previously expected [141, 145, 147, 201] that the structures of complexes of the type $M(L)_2(NO_3)_2$ (L = amine, M = Co(II), Ni(II), Cu(II) and Zn(II)) would bear a close resemblance to that of $(Me_3PO)_2Co(NO_3)_2$ [64] which has symmetrically bidentate nitrate groups in a quasitetrahedral arrangement (Figure I. 3).

However, as yet there are no reported copper(II) nitrate complexes whose structures conform to this. Comparison of the molecular structures of the two forms of $Cu(\alpha\text{-pic})_2(NO_3)_2$ with those of $[Cu(py)_2(NO_3)_2]_2 \cdot py$ [75, 76] (Figure II. 6) and $Cu(NO_3)_2 \cdot 2 \cdot 5H_2O$ [44] (Figure II. 9), reveals that all four complexes are based on a short-bonded square-planar arrangement, with two long-bonded oxygens of the nitrate groups lying below this plane in a cis fashion. This is in contrast to $Cu(C_2H_4N_2)(NO_3)_2$ [46] in which the long-bonded oxygens of the nitrate groups are trans (Figure III. 9). Above the square-plane in both the pyridine and hydrate complexes, there are longer Cu-O bonds which bridge the two monomeric units to effect polymerisation. However, in both forms of $Cu(\alpha\text{-pic})_2(NO_3)_2$, this position is blocked by the presence of the cis α-methyl groups. The cis relationship of the α-methyl groups is also found in $Cu(\alpha\text{-pic})_2Cl_2$ [203] (Figure III. 2), although in this case the smaller steric requirements of chlorine atoms in comparison with nitrate groups, allow a dimerising bond on the opposite side of the square-plane from the methyl groups.

Kettle and Pioli [207] have studied copper(II) acetate complexes of pyridine and α-picoline to examine the effect of steric hindrance of the latter ligand on the coordination of the copper. Since this work, the structures of several complexes of halogen-substituted acetates with α-picoline have been reported, in particular $Cu(\alpha\text{-pic})_2(ClCH_2CO_2)_2$ (A) [204] and $Cu(\alpha\text{-pic})_2(Cl_2CHCO_2)_2$ (B) [208]. The molecular structures of

these two complexes are shown in Figure III. 10 (A and B). The picoline rings are in different orientations in each case with the α-methyl groups lying in trans positions in the former complex and in cis positions in the latter. However, in both complexes the acetate groups are asymmetrically coordinated to the copper with the long Cu-O bonds trans to each other as found in $Cu(C_2H_4N_2)(NO_3)_2$ [46] (Figure III. 9) and in contrast to the cis-configuration of the long Cu-O bonds in both forms of $Cu(\alpha\text{-pic})_2(NO_3)_2$. The two acetate groups are equivalent in (A) as any steric hindrance caused by the α-methyl groups has an equal effect on each acetate in this configuration. However, with the α-methyl groups in cis positions (B), the axial site on the same side of the equatorial plane as these groups is effectively blocked causing a lengthening of the Cu-O bond (2.711(10) Å) in this area. The Cu-O bond trans to this is correspondingly shorter (2.493(9) Å) as there is no blocking of the axial site on this side of the plane. The molecular packing of the latter complex (B) bears a close relationship to the packing in $Cu(\alpha\text{-pic})_2(NO_3)_2$ (Form I), but the different configuration of the acetate and nitrate groups in the two complexes precludes a discussion of the effects on the geometry of the relatively-close intermolecular contacts.

A further basis for comparison lies in the difference in angle between the picoline rings and the equatorial CuN_2O_2 chromophore. In the two forms of $Cu(\alpha\text{-pic})_2(NO_3)_2$ and in $Cu(\alpha\text{-pic})_2(Cl_2CHCO_2)_2$ (B) where the α-methyl groups are in

cis positions, this angle is 75-88°, whereas in $Cu(\alpha\text{-pic})_2(ClCH_2CO_2)_2$ it is decreased to 60°. These values reflect the different stereochemical requirements of the two configurations of the α-methyl groups.

The nitrate groups in both forms of $Cu(\alpha\text{-pic})_2(NO_3)_2$ show polarisation effects as a result of copper-oxygen coordination. This is most clearly evident in Form II where the terminal N-O bonds (N(3)-O(2) 1.21(2), N(4)-O(6) 1.21(2) Å) are just significantly shorter than the N-O bonds associated with the strongest Cu-O interactions (N(3)-O(3) 1.29(2) and N(4)-O(4) 1.29(2) Å). Moreover, the O-N-O valency angles differ from the ideal value of 120° in the expected manner, with the largest angle opposite the shortest copper-oxygen bond. The Cu-O-N angles are also decreased from the value of 110° obtained for normal unidentate coordination [106], and this reflects the strength of the longer copper-oxygen bonds. All the nitrate groups are virtually planar with the copper atoms lying just off these planes (Tables III. II and III. III). The dihedral angles between the planes of the nitrate groups are 10° (Form I) and 6° (Form II).

All the bond lengths and angles within the picoline groups are in good agreement with accepted values [209]. The pyridine rings are planar and, although the α-methyl groups are coplanar with this ring in each case, the copper atoms lie just off these planes (Tables III. II and III. III). The dihedral angles between the pyridine planes are 8° (Form I) and 13° (Form II). The distances

between the α-methyl carbon atoms and the nearest oxygen atoms are all greater than 3.3 Å in both forms and thus, steric effects of the α-methyl groups on the nitrates are either very small or non-existent.

Although the packing arrangements of the two crystalline forms are quite different, there is one feature common to both. In Form I, the nitrate groups are all approximately aligned in the ac plane, and the α-picoline moieties are approximately aligned in the bc plane, whereas, in Form II, the approximate alignment of the nitrate groups corresponds to the bc- and the α-picolines approximately in the ab planes. This may be alternatively stated by considering the local equatorial x and y, and axial z directions, which correspond to the a, b and c directions respectively in Form I, but to the a, c and b directions in Form II. One possible reason why the molecule may pack in two different ways in almost identical unit cells, is that, in addition to being compact, it has virtually identical dimensions in the two directions of the equatorial plane defined by the extent of the α-picoline and nitrate moieties from the central copper atom. It is therefore relatively easy to envisage the nitrate and α-picoline groups adopting alternative positions, especially when the overall alignment of the delocalised planes throughout the crystal is maintained by such a change. In addition, it may be noted that the b and c edges of the two unit cells are all very similar, and it is these lengths which define the localised z-axes of the two crystalline forms.

Although it is difficult to estimate exactly the relative efficiencies of the crystal packing in the two modifications, both forms have exactly the same number of intermolecular contacts < 3.5 Å. There are differences, however, between the structures of the two molecules, in particular the non-equivalence of the nitrate groups in Form I, which may be related to detailed differences in molecular packing. In Form I, O(2) closely approaches both O(4) and C(7) (O(2) . . . O(4) 3.37, O(2) . . . C(7) 3.12 Å) and O(4) is close to C(2) (O(4) . . . C(2) 3.12 Å). In Form II, however, there are no O . . . O intermolecular contacts < 3.59 Å, and no O . . . C contacts < 3.32 Å. Since it is in the detailed nitrate coordination that the molecules most markedly differ, it is reasonable to assume that the crystal-packing in Form I has influenced the molecular geometry to a significant extent.

TABLE III.I

$Cu(\alpha\text{-pic})_2(NO_3)_2$ - Forms I & II

Interatomic distances (Å) and angles (°) for both forms with estimated standard deviations in parentheses

(a) Interatomic Distances

	Form I	Form II
Cu-O(1)	2.307(13)	2.517(8)
Cu-O(3)	2.026(16)	1.983(10)
Cu-O(4)	1.971(13)	2.005(10)
Cu-O(6)	2.489(14)	2.551(7)
Cu-N(1)	2.000(12)	2.000(10)
Cu-N(2)	1.970(12)	1.999(10)
C(1)-N(1)	1.28(2)	1.35(2)
C(1)-C(2)	1.39(2)	1.34(2)
C(1)-C(6)	1.44(2)	1.49(2)
C(2)-C(3)	1.35(2)	1.38(2)
C(3)-C(4)	1.30(2)	1.37(2)
C(4)-C(5)	1.36(2)	1.41(2)
C(5)-N(1)	1.30(2)	1.33(2)
C(7)-N(2)	1.28(2)	1.35(2)
C(7)-C(8)	1.38(3)	1.38(2)
C(7)-C(12)	1.44(2)	1.47(2)
C(8)-C(9)	1.30(2)	1.39(2)
C(9)-C(10)	1.30(3)	1.36(2)
C(10)-C(11)	1.37(2)	1.34(2)
C(11)-N(2)	1.32(2)	1.36(2)
N(3)-O(1)	1.23(2)	1.25(2)
N(3)-O(2)	1.20(2)	1.21(2)
N(3)-O(3)	1.23(2)	1.29(2)
N(4)-O(4)	1.27(2)	1.29(2)
N(4)-O(5)	1.20(2)	1.21(2)
N(4)-O(6)	1.20(2)	1.24(2)

TABLE III.I (cont)

(b) Interbond angles

	Form I	Form II
O(1)-Cu-O(3)	56.0(5)	55.3(4)
O(1)-Cu-O(4)	140.6(5)	129.5(4)
O(1)-Cu-O(6)	89.1(5)	74.8(4)
O(1)-Cu-N(1)	88.2(5)	92.3(4)
O(1)-Cu-N(2)	94.1(5)	94.3(4)
O(3)-Cu-O(4)	163.2(5)	175.1(4)
O(3)-Cu-O(6)	145.1(5)	130.0(4)
O(3)-Cu-N(1)	88.9(6)	90.0(5)
O(3)-Cu-N(2)	90.6(6)	89.4(5)
O(4)-Cu-O(6)	51.7(4)	54.9(4)
O(4)-Cu-N(1)	89.3(5)	88.7(5)
O(4)-Cu-N(2)	90.3(5)	91.2(5)
O(6)-Cu-N(1)	92.2(5)	95.3(4)
O(6)-Cu-N(2)	89.9(5)	91.6(4)
N(1)-Cu-N(2)	176.9(5)	171.5(4)
C(2)-C(1)-C(6)	121.9(14)	121.8(13)
C(2)-C(1)-N(1)	122.7(14)	121.9(12)
C(6)-C(1)-N(1)	115.4(14)	116.3(12)
C(1)-C(2)-C(3)	118.1(15)	120.4(14)
C(2)-C(3)-C(4)	118.8(16)	118.7(14)
C(3)-C(4)-C(5)	119.9(16)	119.0(13)
C(4)-C(5)-N(1)	123.2(15)	120.4(12)
Cu-N(1)-C(1)	122.5(10)	123.6(8)
Cu-N(1)-C(5)	120.4(11)	116.9(9)
C(1)-N(1)-C(5)	117.2(13)	119.5(11)
C(8)-C(7)-C(12)	125.0(17)	122.2(12)
C(8)-C(7)-N(2)	121.1(17)	120.1(11)

TABLE III.I(b) (cont)

	Form I	Form II
C(12)-C(7)-N(2)	113.9(16)	117.6(11)
C(7)-C(8)-C(9)	122.3(19)	121.3(13)
C(8)-C(9)-C(10)	116.2(17)	116.0(13)
C(9)-C(10)-C(11)	122.4(18)	122.3(14)
C(10)-C(11)-N(2)	120.2(16)	121.8(12)
Cu-N(2)-C(7)	125.3(11)	120.8(8)
Cu-N(2)-C(11)	116.9(11)	120.5(9)
C(7)-N(2)-C(11)	117.8(15)	118.5(11)
Cu-O(1)-N(3)	87.5(10)	83.0(8)
Cu-O(3)-N(3)	100.1(11)	107.2(8)
Cu-O(4)-N(4)	111.7(10)	106.5(9)
Cu-O(6)-N(4)	87.6(10)	81.9(8)
O(1)-N(3)-O(2)	129.6(16)	125.3(12)
O(1)-N(3)-O(3)	116.1(15)	114.5(13)
O(2)-N(3)-O(3)	116.3(16)	120.1(12)
O(4)-N(4)-O(5)	124.7(15)	117.4(13)
O(4)-N(4)-O(6)	109.0(14)	116.7(14)
O(5)-N(4)-O(6)	129.3(16)	125.9(13)

TABLE III.I (cont)

(c) Intramolecular non-bonded distances

	Form I	Form II
Cu. . .C(1)	2.90	2.97
Cu. . .C(5)	2.88	2.86
Cu. . .C(6)	3.00	3.14
Cu. . .C(7)	2.90	2.93
Cu. . .C(11)	2.82	2.93
Cu. . .C(12)	3.02	3.08
Cu. . .N(3)	2.55	2.67
Cu. . .N(4)	2.71	2.68
O(1). . .C(5)	3.10	3.39
O(1). . .C(11)	3.13	3.35
O(1). . .O(2)	2.18	2.19
O(1). . .O(3)	2.05	2.14
O(1). . .O(6)	3.37	3.08
O(1). . .N(1)	3.00	3.28
O(1). . .N(2)	3.14	3.33
O(2). . .O(3)	2.06	2.17
O(3). . .C(1)	3.37	3.45
O(3). . .C(6)	3.32	3.31
O(3). . .N(1)	2.82	2.82
O(3). . .N(2)	2.84	2.80
O(4). . .C(5)	3.54	3.29
O(4). . .O(5)	2.17	2.14
O(4). . .O(6)	2.00	2.15
O(4). . .N(1)	2.79	2.80
O(4). . .N(2)	2.79	2.86
O(5). . .O(6)	2.11	2.19
O(6). . .C(5)	3.32	3.21
O(6). . .C(11)	3.25	3.28
O(6). . .N(1)	3.25	3.38
O(6). . .N(2)	3.17	3.29
N(1). . .N(3)	3.16	3.39
N(1). . .N(4)	3.38	3.41
N(2). . .N(3)	3.32	3.38
N(2). . .N(4)	3.37	3.38

TABLE III.I (cont)

(d) Intermolecular distances in Form I

O(1). . .C(4)^{I}	3.30	O(3). . .C(3)^{VI}	3.29
O(1). . .C(12)^{II}	3.50	O(3). . .C(9)^{V}	3.41
O(1). . .O(5)^{III}	3.59	O(4). . .C(2)^{VII}	3.12
O(2). . .C(4)^{II}	3.37	O(4). . .C(6)^{VII}	3.45
O(2). . .C(7)^{IV}	3.12	O(5). . .C(3)^{VIII}	3.54
O(2). . .C(8)^{IV}	3.30	O(5). . .C(9)^{IX}	3.57
O(2). . .C(8)^{V}	3.54	O(5). . .C(10)^{IX}	3.53
O(2). . .C(9)^{V}	3.53	O(6). . .C(3)^{IX}	3.59
O(2). . .C(12)^{IV}	3.42	O(6). . .C(9)^{IX}	3.47
O(2). . .O(4)^{IV}	3.37	O(6). . .C(12)^{II}	3.50
O(2). . .N(2)^{V}	3.56	N(3). . .C(4)^{I}	3.65
O(3). . .C(2)^{VI}	3.53	N(4). . .C(3)^{IX}	3.65

Roman numerals as superscripts refer to the following equivalent positions relative to the reference molecule at x, y, z:

I	-x, 1 - y, -z
II	x, 3/2 - y, -1/2 + z
III	-x, 3/2 - y, -1/2 + z
IV	-1 + x, 3/2 - y, -1/2 + z
V	-x, -1/2 + y, 1/2 - z
VI	-x, 1/2 + y, 1/2 - z
VII	1 - x, 1 - y, 1 - z
VIII	1 - x, 1/2 + y, 1/2 - z
IX	1 - x, -1/2 + y, 1/2 - z

TABLE III.I (cont)

(e) Intermolecular distances in Form II

O(1). . .C(6)^{I}	3.47	O(4). . .C(8)^{VII}	3.59
O(2). . .C(2)^{II}	3.56	O(4). . .C(9)^{VII}	3.32
O(2). . .C(9)^{III}	3.43	O(4). . .C(12)^{VIII}	3.59
O(2). . .C(10)^{IV}	3.42	O(5). . .C(3)^{VI}	3.46
O(2). . .C(11)^{IV}	3.35	O(5). . .C(4)^{IX}	3.41
O(2). . .C(12)^{V}	3.39	O(5). . .C(5)^{IX}	3.28
O(2). . .O(4)^{V}	3.59	O(5). . .O(6)^{IX}	3.61
O(3). . .C(2)^{II}	3.62	O(6). . .C(12)^{X}	3.54
O(3). . .C(3)^{II}	3.33	O(6). . .O(5)^{IX}	3.61
O(3). . .C(9)^{V}	3.50	N(3). . .C(9)^{V}	3.51
O(4). . .C(3)^{VI}	3.49	N(4). . .C(3)^{VI}	3.60

Roman numerals as superscripts refer to the following equivalent positions relative to the reference molecule at x, y, z:

I 1 - x, -1/2 + y, 1/2 - z
II -1 + x, 1/2 - y, -1/2 + z
III 1 + x, y, z
IV -x, -y, -z
V x, 1/2 - y, -1/2 + z
VI -1 + x, y, z
VII 1 + x, 1/2 - y, 1/2 + z
VIII x, 1/2 - y, 1/2 + z
IX 1 - x, -y, 1 - z
X x, 1/2 - y, -1/2 + z

TABLE III.II

$Cu(\alpha\text{-pic})_2(NO_3)_2$ - Form I

Least-squares best planes through the molecule. The equations are in the form $kX' + \ell Y' + mZ' = n$, where X', Y' and Z' are coordinates in Å. Distances of atoms from planes (Å) are given in square brackets.

	k	ℓ	m	n
Plane(1):				
O(1)-(3), N(3)	-0.0684	0.9973	-0.0257	9.7154
O(1) -0.001, O(2) -0.001, O(3) -0.001, N(3) 0.002, Cu -0.061				
Plane(2):				
O(4)-(6), N(4)	-0.0705	-0.9947	-0.0747	-10.1100
O(4) -0.001, O(5) -0.001, O(6) -0.001, N(4) 0.003, Cu 0.059				
Plane(3):				
O(1)-(6), N(3), N(4)	-0.0072	-0.9997	-0.0242	-9.7858
O(1) -0.021, O(2) 0.101, O(3) -0.085, O(4) 0.017, O(5) 0.073, O(6) -0.091, N(3) -0.001, N(4) 0.007, Cu -0.062				
Plane(4):				
C(1)-(6), N(1)	-0.9981	0.0160	-0.0593	-1.6813
C(1) 0.015, C(2) -0.004, C(3) -0.019, C(4) 0.026, C(5) -0.003, C(6) 0.006, N(1) -0.021, Cu -0.065				
Plane(5):				
C(7)-(12), N(2)	0.9956	-0.0608	-0.0712	0.8586
C(7) 0.017, C(8) -0.011, C(9) 0.016, C(10) -0.011, C(11) -0.016, C(12) -0.016, N(2) 0.022, Cu 0.081				

TABLE III.II (cont)

	k	ℓ	m	n
Plane(6):				
O(3), O(4), N(1), N(2)	0.0104	0.0431	-0.9990	-2.5255

O(3) -0.117, O(4) -0.120, N(1) 0.119, N(2) 0.118, Cu 0.172, C(6) -2.174, C(12) -2.162, O(1) 1.879, O(6) 1.872

Dihedral angles between planes (°)

Plane (1)-(2)	10	Plane (2)-(5)	90
Plane (1)-(4)	85	Plane (4)-(5)	8
Plane (1)-(5)	83	Plane (4)-(6)	87
Plane (2)-(4)	87	Plane (5)-(6)	86

TABLE III.III

$Cu(\alpha\text{-pic})_2(NO_3)_2$ - Form II

Least-squares best planes through the molecule. The equations are in the form $k\underline{X}' + \ell\underline{Y}' + m\underline{Z}' = n$, where $\underline{X}'$, $\underline{Y}'$ and $\underline{Z}'$ are coordinates in Å. Distances of atoms from planes (Å) are given in square brackets.

	$\underline{k}$	$\underline{\ell}$	$\underline{m}$	$\underline{n}$
Plane(1):				
O(1)-(3), N(3)	0.9905	0.0007	-0.1377	1.7617
O(1) -0.006, O(2) -0.005, O(3) -0.005, N(3) 0.017, Cu -0.094				
Plane(2):				
O(4)-(6), N(4)	0.9935	-0.0846	-0.0768	1.6718
O(4) -0.003, O(5) -0.003, O(6) -0.003, N(4) 0.009, Cu -0.082				
Plane(3):				
O(1)-(6), N(3), N(4)	0.9951	-0.0439	-0.0887	1.6758
O(1) 0.081, O(2) -0.057, O(3) -0.026, O(4) 0.045, O(5) -0.036, O(6) -0.031, N(3) 0.021, N(4) 0.002, Cu -0.006				
Plane(4):				
C(1)-(6), N(1)	-0.0785	-0.1572	-0.9844	-2.7043
C(1) 0.003, C(2) -0.009, C(3) -0.003, C(4) 0.018, C(5) -0.020, C(6) 0.002, N(1) 0.009, Cu 0.013				
Plane(5):				
C(7)-(12), N(2)	-0.0317	0.0561	-0.9979	-2.1937
C(7) -0.014, C(8) 0.011, C(9) -0.018, C(10) 0.018, C(11) 0.002, C(12) 0.011, N(2) -0.010, Cu 0.106				

TABLE III.III (cont)

	k	ℓ	m	n
Plane(6):				
O(3), O(4), N(1), N(2)	-0.0284	-0.9948	-0.0978	-2.9029

O(3) 0.032, O(4) 0.032, N(1) -0.032, N(2) -0.032, Cu 0.115, C(6) -2.368, C(12) -2.425, O(1) 2.121, O(6) 2.136

Dihedral angles between planes (°)

Plane (1)-(2)	6	Plane (2)-(5)	88
Plane (1)-(4)	87	Plane (4)-(5)	13
Plane (1)-(5)	84	Plane (4)-(6)	88
Plane (2)-(4)	89	Plane (5)-(6)	75

FIGURE III.5

$Cu(\alpha\text{-pic})_2(NO_3)_2$ - Form I

A view of the molecule along b showing the atomic numbering

(Unnamed atoms are carbons)

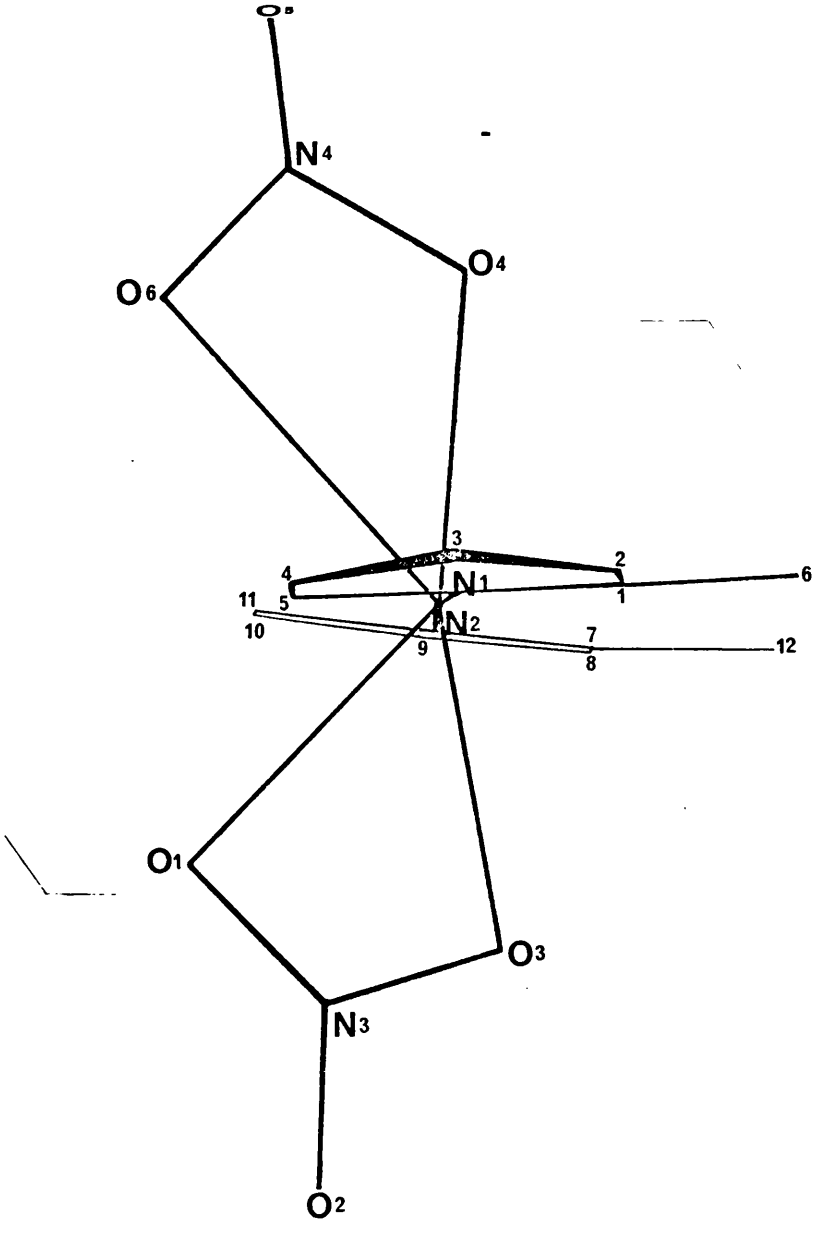

O5
N4
O6
O4
3
2
4
N1
6
11
5
1
N2
10
7
12
9
8
O1
O3
N3
O2

TABLE III.6

$Cu(\alpha\text{-pic})_2(NO_3)_2$ - Form II

A view of the molecule along b showing the atomic numbering

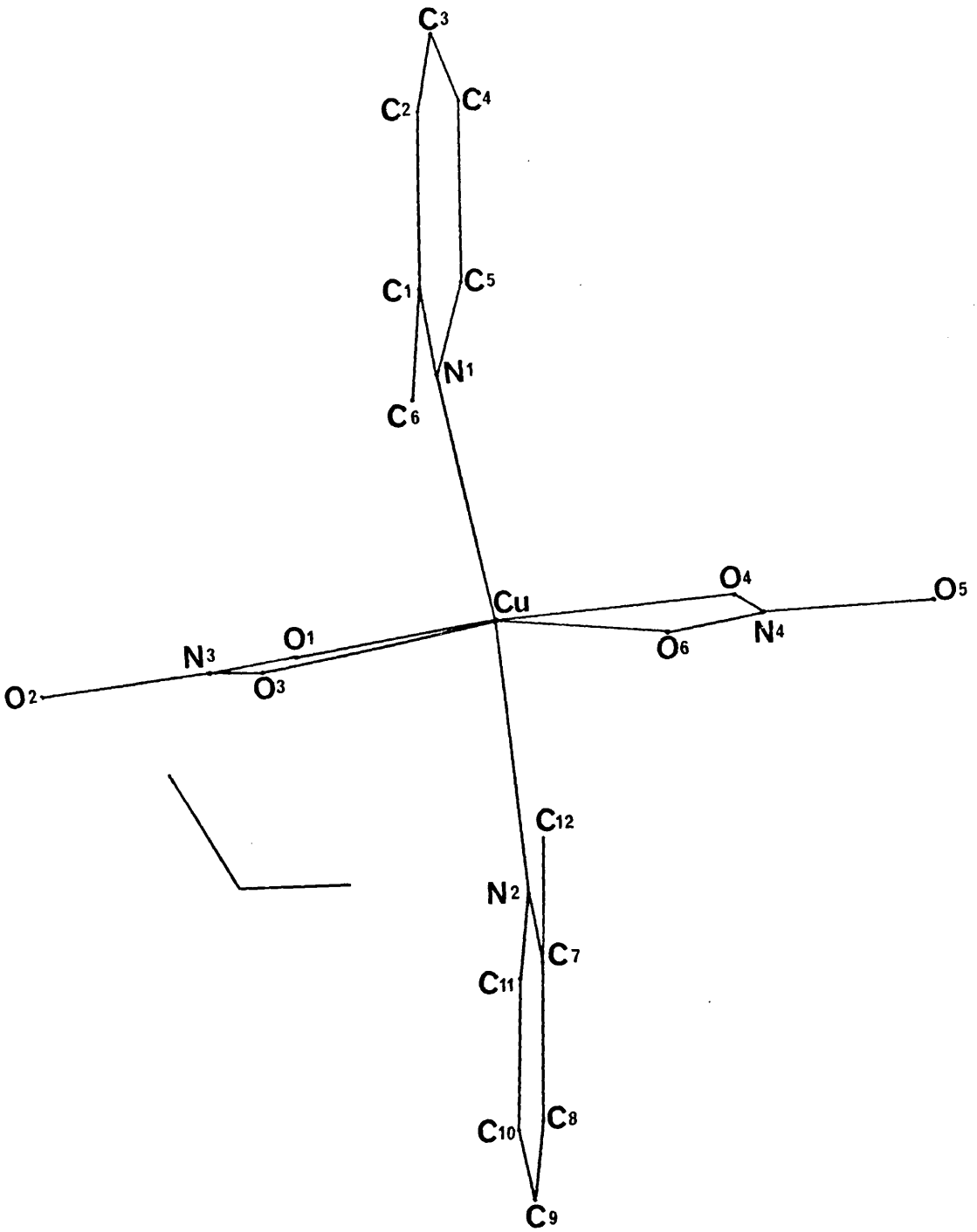

C3
C2
C4
C1
C5
N1
C6
Cu
O4
O5
N3
O1
O6
N4
O2
O3
C12
N2
C7
C11
C10
C8
C9

FIGURE III.7

$Cu(\alpha\text{-pic})_2(NO_3)_2$ - Form I

The molecular packing viewed along the b axis

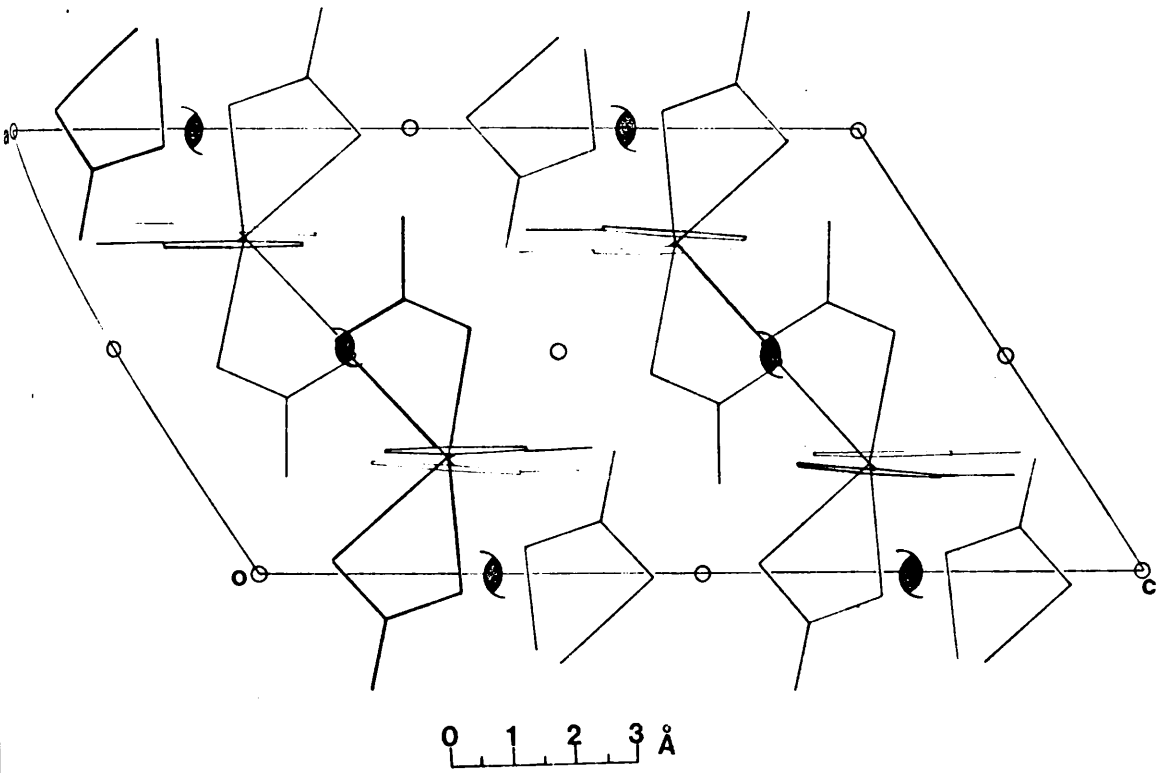
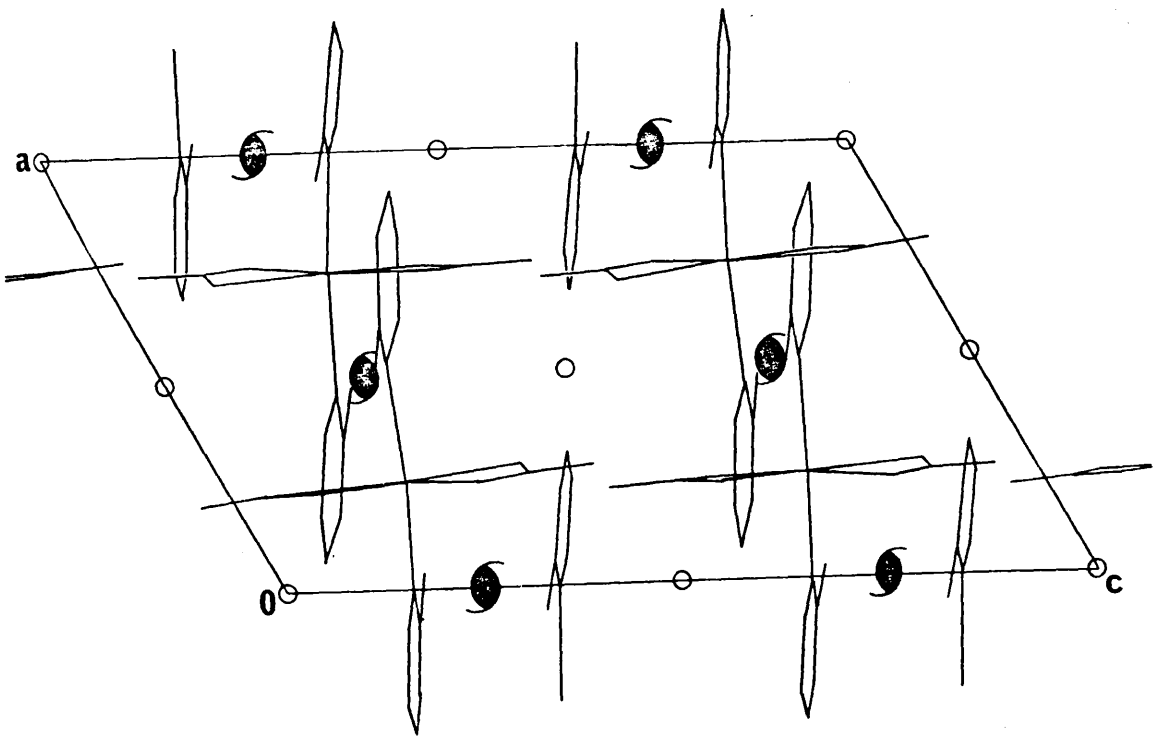

a
o
c
0 1 2 3 Å

FIGURE III.8

$Cu(\alpha\text{-pic})_2(NO_3)_2$ - Form II

The molecular packing viewed along the b axis


a
0
c

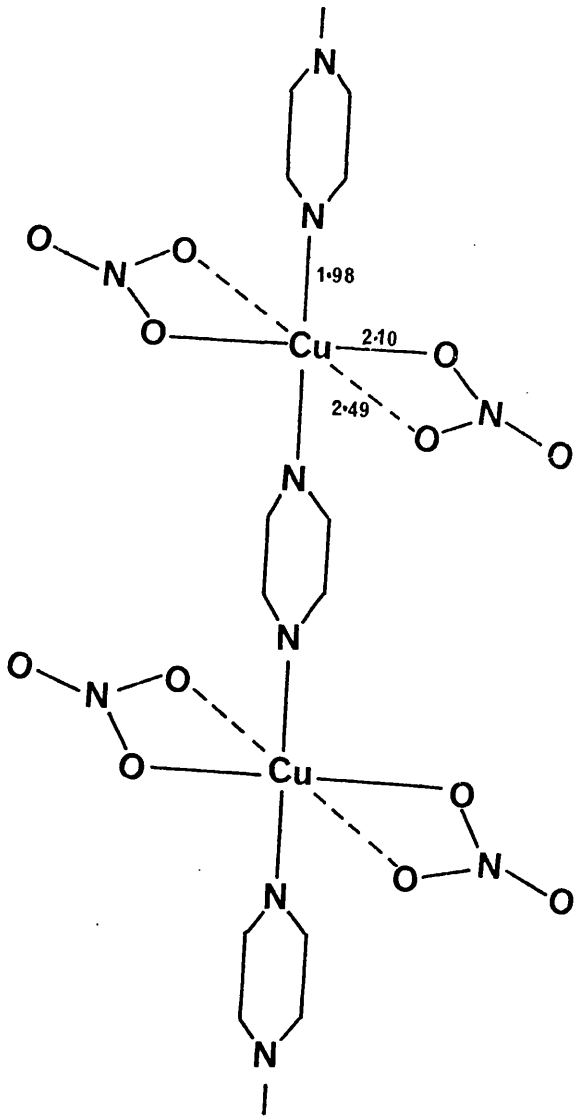


FIGURE III.9

Molecular Structure of $Cu(pyrazine)(NO_3)_2$ (46)

CHAPTER 2

Aquo(dinitratobisquinoline)-cadmium(II)

III. 2. 1. THE CADMIUM NITRATE-QUINOLINE SYSTEM

Quinoline complexes of the type $M(quin)_2(NO_3)_2$ (M = Co(II), Ni(II), Cu(II) and Zn(II)) have been examined and it was suggested that they had structures closely-related to $(Me_3PO)_2Co(NO_3)_2$ (64, 201). It might also be expected that the corresponding Cd(II) complex would belong to this structural type although a polymeric species involving bridging nitrate groups is also a possibility. However, attempts to obtain this anhydrous species proved unsuccessful; the only crystalline complex which resulted being $Cd(quin)_2(NO_3)_2(H_2O)$. The crystal structure of the latter complex was therefore determined to see if any information about the parent compound could be gained. Another reason for this study was to examine the geometry of the nitrate group in the presence of water and a 'bulky' ligand in comparison with the structure of $Ni(py)_2(NO_3)_2(H_2O)_2$ [95] which had been studied earlier (Section II. 1. 6).

III.2.2 CRYSTAL AND MOLECULAR STRUCTURE OF AQUO(DINITRATOBISQUINOLINE)-CADMIUM(II)

III. 2. 2. CRYSTAL AND MOLECULAR STRUCTURE OF AQUO(DINITRATOBISQUINOLINE)-CADMIUM(II)

(a) Material Used in the Determination

The complex was prepared by standard literature methods [201] and recrystallised from ethanol-2, 2'-dimethoxypropane mixture.

(b) Experimental and Results

Full experimental details, atomic parameters, thermal parameters and structure-factor tables are given in Appendix VII.

Figures III. 11 and III. 12 show the atomic numbering scheme and molecular packing respectively. The interatomic dimensions are given in Table III. IV and Table III. V gives some least-squares, best planes calculated through the molecule.

(c) Discussion

The analysis has revealed a seven-coordinate, monomeric structure in which the cadmium is surrounded by two non-equivalent bidentate nitrate groups, two quinoline functions and a water molecule. One of these nitrate groups is symmetrically bidentate whilst the other shows a slight asymmetry [(M-O(5) - M-O(4)) = δ = 0.17 Å] which is of the same order as that found in $Cd(NO_3)_2(H_2O)_4$ [44a] (δ = 0.14 Å), $UO_2(NO_3)_2(Et_3PO)_2$

[35] (δ = 0.14 Å), $UO_2(NO_3)_2(H_2O)_2$ [62] (δ = 0.2 Å), and $Zn(py)_3(NO_3)_2$ [80, 81] (δ = 0.19 Å). The cadmium-oxygen (Cd-O(nitrate) 2.393-2.559 Å, Cd-O(water) 2.346 Å) and cadmium-nitrogen (Cd-N 2.296(7), 2.330(7) Å) bond lengths are in accord with previously published values for these lengths in 7 and 8-coordinate cadmium complexes [210], although they are slightly longer than those distances normally found in complexes containing, 4, 5 and six-coordinate cadmium(II). This lengthening is usually explained as being a result of the increased coordination sphere of the cadmium [44a, 52, 73, 80, 81].

The geometry around the cadmium is very distorted and may be described in a number of ways. The structures of the anhydrous complexes $M(quin)_2(NO_3)_2$ (M = Co(II), Ni(II), Cu(II) and Zn(II)) were predicted [201] to be very similar to the pseudotetrahedral geometry of $(Me_3PO)_2Co(NO_3)_2$ [64] (Figure I. 3). If the present complex is regarded as the hydrated species of this structural type, then the nitrate groups and quinoline moieties may be regarded as being arranged in a distorted pseudotetrahedral fashion around the cadmium with the water molecule coordinating on that side of the cadmium atom least affected by the steric bulk of the quinoline groups. Although this is a fairly arbitrary picture, it does reflect the increase in coordination from Zn to Cd, as, in the tetrahedral structure of $Zn(py)_2(NO_3)_2$ [96] (Section II. 1. 4), the nitrate groups are unidentate whereas bidentate nitrate groups are found in the present case. The main justification for

using this pseudotetrahedral approach is the cis positioning of the quinoline groups in contrast to the trans arrangement usually found in non-tetrahedral complexes containing N-heterocyclic ligands.

If the stereochemistry around the cadmium is examined in a more orthodox manner, it may be described as very-distorted, square-based pyramidal, the nitrate groups being regarded as large unidentate anions [64, 73]. Alternatively a more realistic approach is to consider the distortions of the atoms from a pentagonal-bipyramid geometry. Two different views of the coordination around the cadmium are given in Figures III. 13 and III. 14 to show this stereochemistry. The axial sites are occupied by the oxygen of the water [O(7)] and the nitrogen of one of the quinolines [N(2)] while in the equatorial plane lie the nitrogen of the remaining quinoline [N(1)] and the coordinated oxygens of the two nitrate groups [O(1), O(2), O(4) and O(5)]. The latter four oxygens are virtually co-planar with the cadmium atom (maximum deviation from the best least-squares plane = 0. 16 Å). However, N(1) is displaced 0. 88 Å from this plane (Table III. V) the displacement being in the direction away from the axial quinoline ring. The angular distortions in the equatorial plane are shown in Figure III. 15(a). The angles made by the coordinated oxygens of each nitrate group at the cadmium are restricted to ca. 52° by the nitrate geometry. This contraction from the ideal value for a pentagonal plane of 72°, requires an expansion of the other angles and it is not surprising that the largest increases in angles involve the nitrogen atom,

N(1) (O-Cd-N $\sim 92^{o}$), as a result of the steric effects of this quinoline group. By comparison, in the corresponding pentagonal plane of $Cd(py)_3(NO_3)_2$ [71] (Section II. 2. 3), the angle at the cadmium atom between the coordinated oxygens of the nitrate groups is also 52^{o}, but the O-Cd-N angles in this plane (82^{o}) are less than the 0(1)-Cd-0'(1) angle (93^{o}) of the present complex because of the smaller steric requirements of the pyridine molecule.

The atoms N(3) and 0(7) (Figures III. 13 and III. 14) are distorted from the axial sites such that N(3)-Cd-0(7) = $161.5(2)^{o}$. This distortion again is due to steric repulsion between the quinoline groups and both of these atoms lie at an angle away from the ring (A) (Figure III. 11). Deviations from 90^{o} of the angles made at the cadmium between N(2) and 0(7) and the equatorial atoms are given in Figure III. 15(b).

There is the possibility of an extensive hydrogen-bonding network between neighbouring molecules of the present complex. The oxygen atom of the coordinated water is involved in hydrogen bonds with two oxygen atoms from <u>different</u> nitrate groups of <u>different</u> molecules (Figure III. 16). The 0 . . . 0 contacts are 2.80 and 2.84 Å, and the 0'(4) . . 0(7) . . 0''(2) angle is 109.2^{o}. The hydrogen bonding therefore involves the coordinated oxygens of the nitrate groups 0(4) and 0(2) unlike the hydrogen bonding in $Ni(py)_2(NO_3)_2(H_2O)_2$ (Section II. 1. 6) [95] where it is the terminal oxygens that are concerned. However, hydrogen bonding to coordinated oxygens in $Cd(NO_3)_2(H_2O)_4$ [44a] is likely.

although the O . . . O contacts in this case are longer (2.87-2.96 Å) than those found in $Cd(quin)_2(NO_3)_2(H_2O)$. The hydrogen-bonding network in the present complex is 'layered' and approximately aligned in the ab plane. This type of alignment was also a feature in the crystal structure of $Ni(py)_2(NO_3)_2(H_2O)_2$ [95].

The slight differences in coordination of the nitrate groups are reflected in their internal dimensions. The nitrate group showing the greatest asymmetry in its bonding to the cadmium (O(4)-(6), N(4)), has the expected [106] order of N-O bond lengths, N(4)-O(4)>N(4)-O(5)>N(4)-O(6) (1.287(10), 1.252(11), 1.209(8) Å respectively), reflecting the strength of the cadmium-oxygen interaction. Similarly, the O-N-O angles vary from the trigonal value of 120° in the predicted manner suggesting a slight systematic distortion caused by the nitrate coordination. In the other nitrate group (O(1)-(3), N(3)), although the N-O distance adjacent to the strongest Cd-O interaction is increased from the free ion value [103] (N(3)-O(2) 1.289(11) Å), the remaining N-O distances are experimentally identical (N(3)-O(1) 1.233(10), N(3)-O(3) 1.235(11) Å). If the latter result is genuine, the most obvious cause is some intermolecular effect since the coordinated oxygens of each nitrate group at the cadmium are restricted to ca. 52° by the nitrate geometry. This contraction from the ideal value for a pentagonal plane of 72°, requires an expansion of the other angles and it is not surprising that the largest increases in angles involve the nitrogen atom, N(1) (O-Cd-N ~ 92°), as a result

of the steric effects of this quinoline group. By comparison, in the corresponding pentagonal plane of $Cd(py)_3(NO_3)_2$ [71] (Section II. 2. 3), the angle at the cadmium atom between the coordinated oxygens of the nitrate groups is also 52°, but the 0-Cd-N angles in this plane (82°) are less than the 0(1)-Cd-0'(1) angle (93°) of the present complex because of the smaller steric requirements of the pyridine molecule.

The atoms N(3) and 0(7) (Figures III. 13 and III. 14) are distorted from the axial sites such that N(3)-Cd-0(7) = 161. 5(2)°. This distortion again is due to steric repulsion between the quinoline groups and both of these atoms lie at an angle away from the ring (A) (Figure III. 11). Deviations from 90° of the angles made at the cadmium between N(2) and 0(7) and the equatorial atoms are given in Figure III. 15(b).

There is the possibility of an extensive hydrogen-bonding network between neighbouring molecules of the present complex. The oxygen atom of the coordinated water is involved in hydrogen bonds with two oxygen atoms from <u>different</u> nitrate groups of <u>different</u> molecules (Figure III. 16). The 0 . . . 0 contacts are 2. 80 and 2. 84 Å and the 0'(4) . . 0(7) . . 0''(2) angle is 109. 2°. The hydrogen nitrate geometry is known to be sensitive to changes in crystal packing (see $Cu(\alpha\text{-pic})_2(NO_3)_2$ - Section III. 1. 2 [77-9]). The oxygen atom of the water molecule 0(7) has an intermolecular contact with 0(3) of 3. 26 Å, whereas the shortest 0 . . . 0 inter-molecular distance involving 0(6) is 3. 46 Å. Although both of these

values are larger than the sums of the van der Waals radii of two oxygen atoms (2.80 Å [108]) this may be the reason for the slight distortions in the second nitrate group. The O-N-O angles in the latter nitrate group do show the expected order, with the largest angle opposite the strongest Cd-O bond.

Consideration of the Cd-O-N angles reflect the different cadmium-oxygen interactions in the two nitrate groups. In both cases, the nitrates are planar (Table III. IV) although, in the former case, the cadmium atom is significantly off this plane (0.32 Å), whereas, in the latter nitrate group, the cadmium atom is virtually coplanar with the four atoms (O(1)-(3), N(3)). This difference probably results from intramolecular steric effects. The dihedral angle between the nitrate planes is 18°.

The internal dimensions of the quinoline rings are in accord with literature values [211]. Both groups are planar although in neither case is the cadmium atom coplanar with the rings (Table III. V). Again, this is expected to arise because of stereochemical considerations in packing these bulky ligands around the cadmium atom. The dihedral angle between the quinoline groups is 71°.

TABLE III.IV

$Cd(quin)_2(NO_3)_2(H_2O)$

Interatomic distances (Å) and angles (°) with estimated standard deviations in parentheses.

(a) Bonded distances

Cd-O(1)	2.492(7)	C(10)-N(2)	1.305(11)
Cd-O(2)	2.430(8)	C(10)-C(11)	1.439(13)
Cd-O(4)	2.393(7)	C(11)-C(12)	1.394(11)
Cd-O(5)	2.559(9)	C(12)-C(13)	1.385(14)
Cd-O(7)	2.346(7)	C(13)-C(14)	1.417(14)
Cd-N(1)	2.296(7)	C(13)-C(18)	1.426(13)
Cd-N(2)	2.330(7)	C(14)-C(15)	1.343(15)
C(1)-N(1)	1.318(10)	C(15)-C(16)	1.400(15)
C(1)-C(2)	1.407(12)	C(16)-C(17)	1.391(13)
C(2)-C(3)	1.340(14)	C(17)-C(18)	1.431(12)
C(3)-C(4)	1.460(13)	C(18)-N(2)	1.382(11)
C(4)-C(5)	1.406(13)	N(3)-O(1)	1.233(10)
C(4)-C(9)	1.411(12)	N(3)-O(2)	1.289(11)
C(5)-C(6)	1.353(15)	N(3)-O(3)	1.235(11)
C(6)-C(7)	1.370(15)	N(4)-O(4)	1.287(10)
C(7)-C(8)	1.363(15)	N(4)-O(5)	1.252(11)
C(8)-C(9)	1.402(13)	N(4)-O(6)	1.209(8)
C(9)-N(1)	1.389(11)	Mean C-H	0.95
		Mean O-H	0.85

TABLE III.IV (cont)

(b) Interbond angles

O(1)-Cd-O(2)	52.0(2)	C(6)-C(7)-C(8)	120.9(9)
O(1)-Cd-O(4)	74.8(2)	C(7)-C(8)-C(9)	119.8(8)
O(1)-Cd-O(5)	124.0(2)	C(8)-C(9)-C(4)	118.4(8)
O(1)-Cd-O(7)	80.2(2)	C(4)-C(9)-N(1)	121.4(8)
O(1)-Cd-N(1)	144.1(2)	C(8)-C(9)-N(1)	120.2(8)
O(1)-Cd-N(2)	81.4(2)	Cd-N(2)-C(10)	116.8(8)
O(2)-Cd-O(4)	126.2(3)	Cd-N(2)-C(18)	125.3(5)
O(2)-Cd-O(5)	173.0(3)	C(10)-N(2)-C(18)	117.8(7)
O(2)-Cd-O(7)	81.9(2)	C(11)-C(10)-N(2)	124.7(8)
O(2)-Cd-N(1)	93.1(3)	C(10)-C(11)-C(12)	116.7(9)
O(2)-Cd-N(2)	87.4(2)	C(11)-C(12)-C(13)	120.6(9)
O(4)-Cd-O(5)	51.3(3)	C(12)-C(13)-C(14)	122.7(9)
O(4)-Cd-O(7)	82.4(3)	C(12)-C(13)-C(18)	118.2(8)
O(4)-Cd-N(1)	137.0(3)	C(14)-C(13)-C(18)	119.1(8)
O(4)-Cd-N(2)	92.0(2)	C(13)-C(14)-C(15)	120.8(9)
O(5)-Cd-O(7)	103.5(3)	C(14)-C(15)-C(16)	121.5(9)
O(5)-Cd-N(1)	91.6(3)	C(15)-C(16)-C(17)	120.4(9)
O(5)-Cd-N(2)	86.2(3)	C(16)-C(17)-C(18)	119.3(8)
O(7)-Cd-N(1)	87.5(2)	C(17)-C(18)-C(13)	119.8(8)
O(7)-Cd-N(2)	161.5(2)	C(13)-C(18)-N(2)	122.0(7)
N(1)-Cd-N(2)	108.2(3)	C(17)-C(18)-N(2)	119.1(8)
Cd-N(1)-C(1)	116.7(5)	Cd-O(1)-N(3)	94.5(5)
Cd-N(1)-C(9)	125.3(6)	Cd-O(2)-N(3)	96.0(5)
C(1)-N(1)-C(9)	117.7(7)	Cd-O(4)-N(4)	99.9(5)
C(2)-C(1)-N(1)	125.7(8)	Cd-O(5)-N(4)	92.9(6)
C(1)-C(2)-C(3)	117.5(8)	O(1)-N(3)-O(2)	117.6(8)
C(2)-C(3)-C(4)	120.8(8)	O(1)-N(3)-O(3)	123.6(8)
C(3)-C(4)-C(5)	122.9(8)	O(2)-N(3)-O(3)	118.9(8)
C(3)-C(4)-C(9)	116.9(7)	O(4)-N(4)-O(5)	115.5(7)
C(5)-C(4)-C(9)	120.2(8)	O(4)-N(4)-O(6)	120.4(8)
C(4)-C(5)-C(6)	118.6(9)	O(5)-N(4)-O(6)	124.1(8)
C(5)-C(6)-C(7)	122.0(9)	H(19)-O(7)-H(20)	104(8)

Mean C-C-H 119

Mean N-C-H 116

O'(4). .O(7). .O"(2) 109.2(8)

TABLE III.IV (cont)

(c) Intramolecular distances for non-hydrogen atoms

Cd. . .C(1)	3.12	O(2). . .O(7)	3.13
Cd. . .C(8)	3.49	O(2). . .N(1)	3.43
Cd. . .C(9)	3.30	O(2). . .N(2)	3.29
Cd. . .C(10)	3.14	O(4). . .C(10)	3.25
Cd. . .C(17)	3.49	O(4). . .O(5)	2.15
Cd. . .C(18)	3.32	O(4). . .O(6)	2.17
Cd. . .N(3)	2.87	O(4). . .O(7)	3.12
Cd. . .N(4)	2.90	O(4). . .N(2)	3.40
O(1). . .O(2)	2.16	O(5). . .C(8)	3.16
O(1). . .O(3)	2.18	O(5). . .C(10)	3.48
O(1). . .O(4)	2.97	O(5). . .O(6)	2.17
O(1). . .O(7)	3.12	O(5). . .N(1)	3.49
O(1). . .N(2)	3.15	O(5). . .N(2)	3.35
O(2). . .C(17)	3.34	O(7). . .C(1)	3.16
O(2). . .O(3)	2.17	O(7). . .N(1)	3.21
N(2). . .N(3)	3.49	O(7). . .N(3)	3.38

TABLE III.IV (cont)

(d) Intermolecular contacts, including those involved in hydrogen bonding

O(1). . .C(1)^{I}	3.34	O(4). . .O(7)^{I}	2.84
O(1). . .C(2)^{I}	3.44	O(4). . .N(3)^{I}	3.30
O(1). . .C(14)^{II}	3.36	O(4). . .H(19)^{I}	1.97
O(1). . .C(15)^{II}	3.42	O(5). . .C(5)^{VI}	3.42
O(2). . .O(4)^{III}	3.19	O(6). . .C(1)^{VII}	3.00
O(2). . .O(7)^{III}	2.80	O(6). . .C(2)^{VII}	3.26
O(2). . .H(20)^{III}	2.03	O(6). . .C(17)^{VII}	3.37
O(3). . .C(5)^{IV}	3.31	O(6). . .O(7)^{I}	3.42
O(3). . .C(12)^{V}	3.43	O(6). . .N(1)^{VII}	3.39
O(3). . .O(7)^{III}	3.26	O(7). . .N(3)^{I}	3.43

Roman numerals as superscripts refer to the following equivalent positions with respect to the reference molecule at x, y, z:

I	-x, 1/2 + y, 1/2 - z
II	1 - x, 1/2 + y, 1/2 - z
III	-x, -1/2 + y, 1/2 - z
IV	x, -1/2 - y, -1/2 + z
V	1 - x, -1/2 + y, 1/2 - z
VI	-x, -y, 1 - z
VII	x, 1 + y, z

TABLE III.V

$Cd(quin)_2(NO_3)_2(H_2O)$

Least-squares best planes through the molecule. The equations are in the form $kX' + \ell Y' + mZ' = n$, where X', Y' and Z' are coordinates in Å. Distances of atoms from planes (Å) are given in square brackets

	k	ℓ	m	n
Plane(1):				
C(1)-(9), N(1)	0.6514	-0.7341	-0.1916	-0.4986

C(1) 0.003, C(2) 0.018, C(3) 0.007, C(4) -0.006, C(5) -0.012, C(6) -0.011, C(7) 0.018, C(8) 0.017, C(9) -0.005, N(1) -0.030, Cd -0.311

Plane(2):

C(10)-(18), N(2)	-0.0796	-0.2728	-0.9588	-7.6850

C(10) -0.004, C(11) -0.009, C(12) 0.005, C(13) -0.004, C(14) 0.010, C(15) -0.002, C(16) -0.007, C(17) 0.001, C(18) -0.004, N(2) 0.014, Cd 0.210

Plane(3):

O(1)-(3), N(3)	-0.9877	0.0251	-0.1542	-2.5963

O(1) -0.002, O(2) -0.002, O(3) -0.002, N(3) 0.005, Cd -0.036

Plane(4):

O(4)-(6), N(4)	0.9852	-0.0926	-0.1440	0.0318

O(4) 0.002, O(5) 0.002, O(6) 0.002, N(4) -0.005, Cd 0.318

Dihedral angles (°) between planes

Plane (1)-(2)	71	Plane (2)-(3)	77
Plane (1)-(3)	51	Plane (2)-(4)	85
Plane (1)-(4)	43	Plane (3)-(4)	18

FIGURE III.11

$Cd(quin)_2(NO_3)_2(H_2O)$

A view of the molecule along a showing the atomic numbering

(Unnamed atoms are carbons)

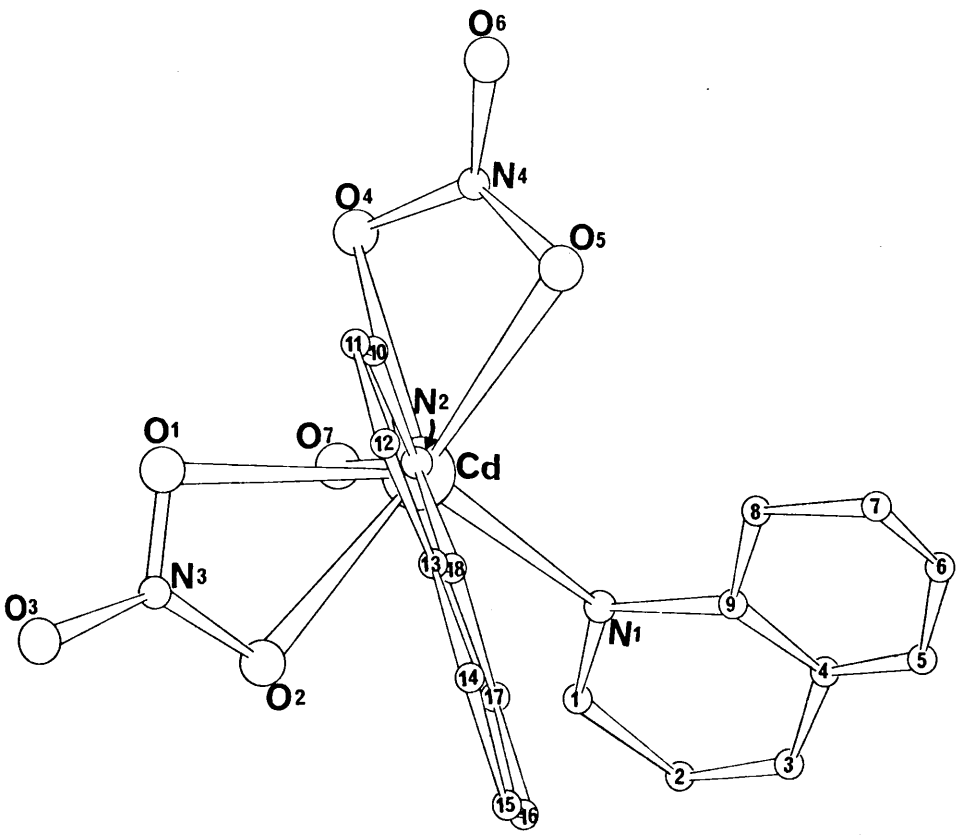

O6
N4
O4
O5
11
10
N2
O1
O7
12
Cd
8
7
13
18
N3
6
9
O3
N1
5
4
14
17
1
O2
2
3
15
16

FIGURE III.12

$Cd(quin)_2(NO_3)_2(H_2O)$

The molecular packing viewed along the b axis

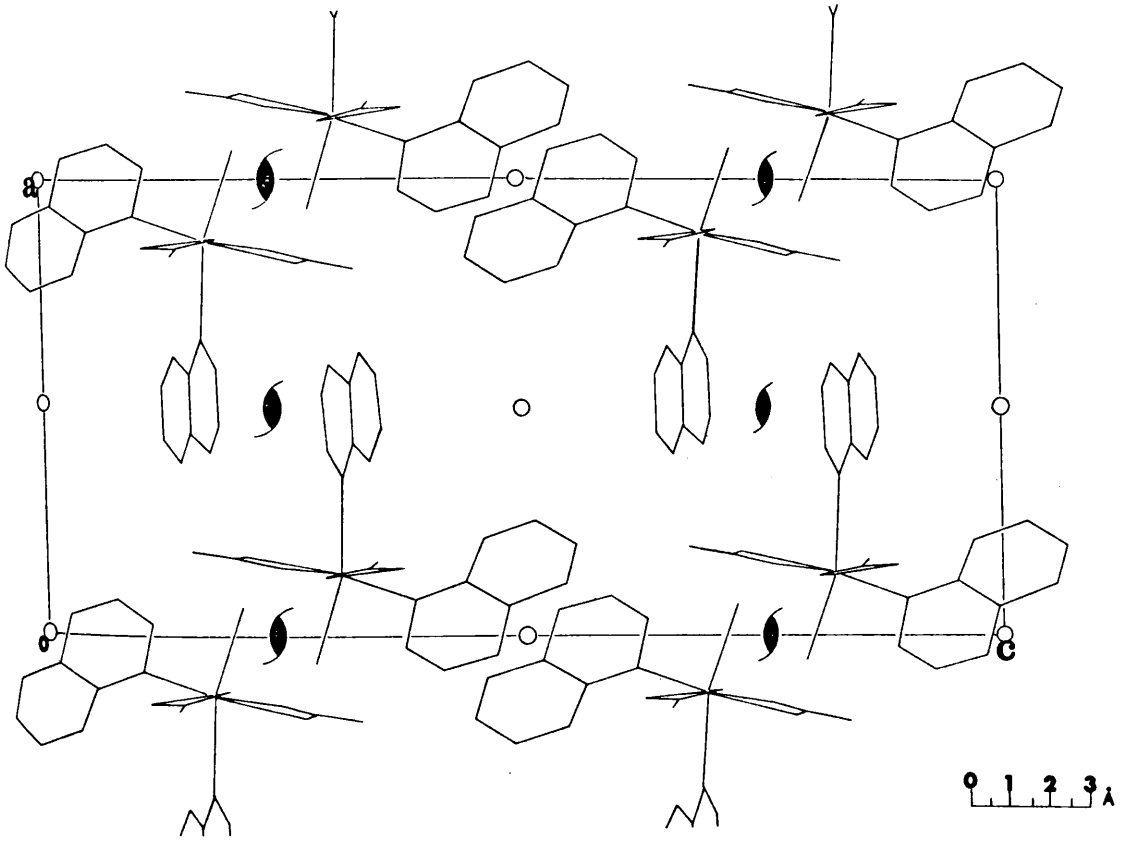

a
c
0 1 2 3 Å

FIGURE III.13

The environment around the cadmium atom viewed along c

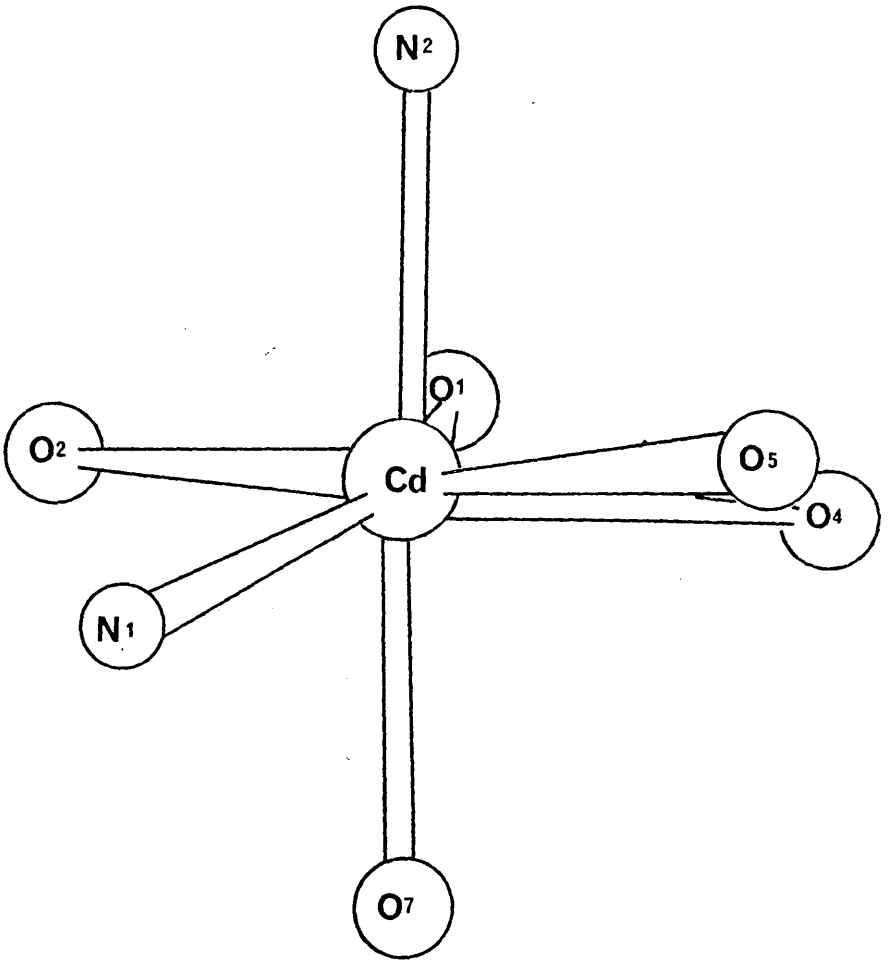


FIGURE III.14

The environment around the cadmium atom viewed along a

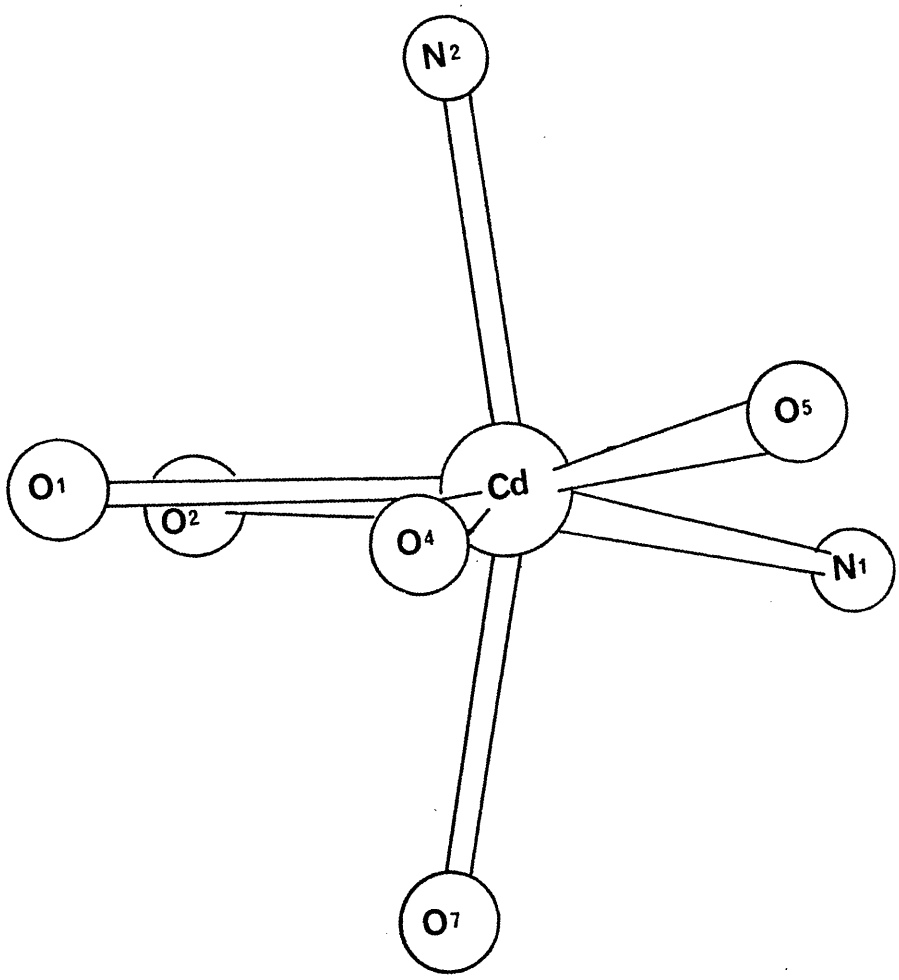
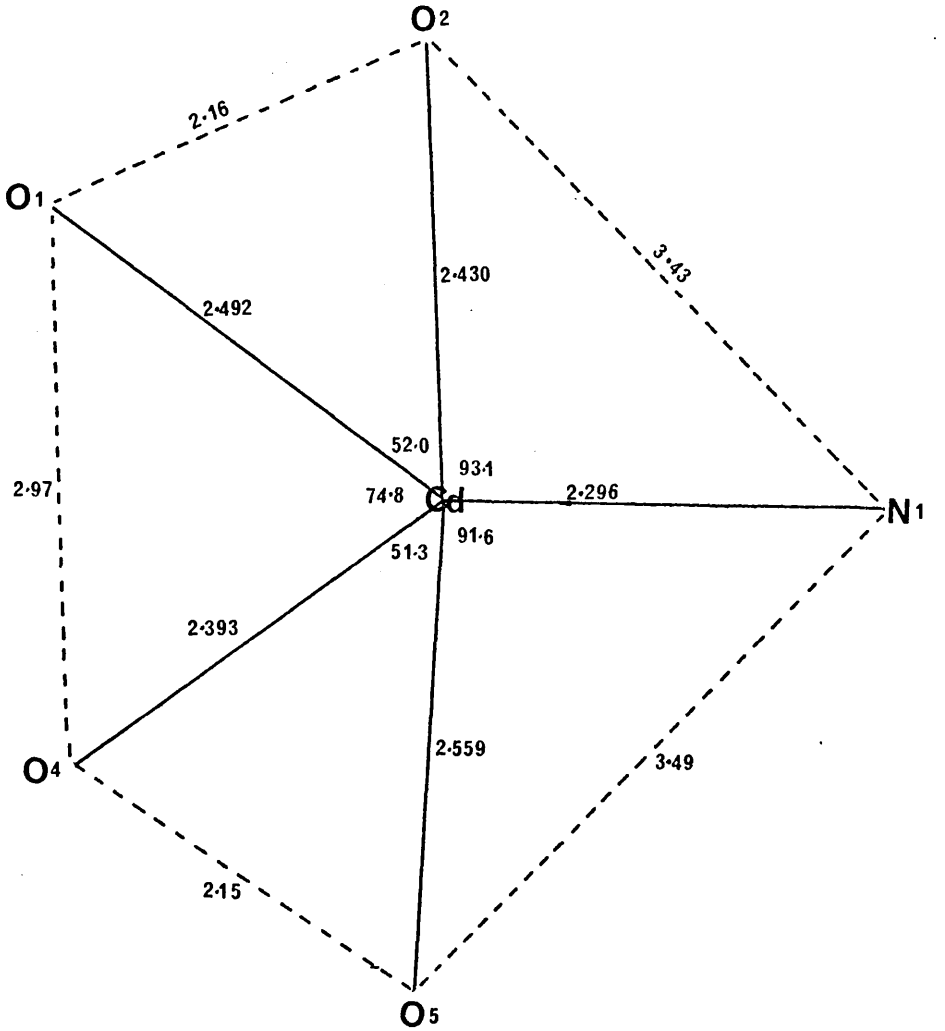


FIGURE III.15

(a)



(b)

Deviations of angles between equatorial atoms and axial atoms from 90°

	X-Cd-N(2)	X-Cd-O(7)
N(1)	108.2	87.5
O(2)	87.4	81.9
O(1)	81.4	80.2
O(4)	92.0	82.4
O(5)	86.2	103.5

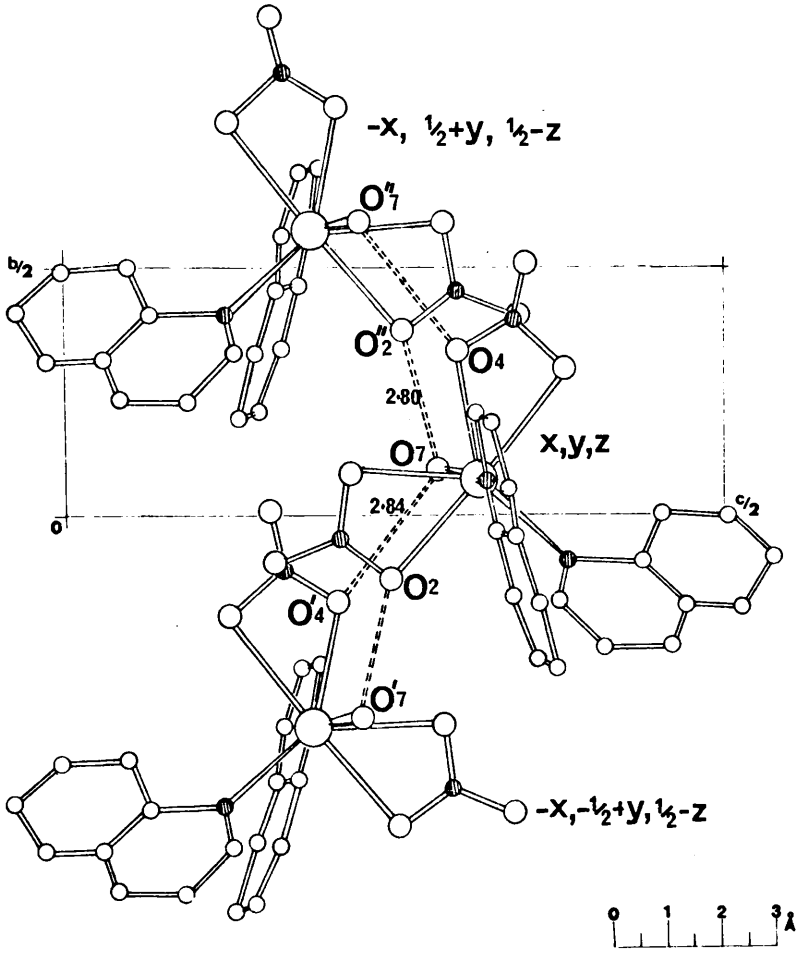
Deviation of angle at cadmium atom from 180°

$$N(2)\text{-}Cd\text{-}O(7) = 161.5^{\circ}$$

FIGURE III.16

$Cd(quin)_2(NO_3)_2(H_2O)$

The structure viewed along a showing the hydrogen bonding


-x, ½+y, ½-z
O''7
b/2
O''2
O4
2·80
O7
x,y,z
2·84
c/2
0
O2
O'4
O'7
-x,-½+y,½-z
0 1 2 3 Å

APPENDICES

APPENDICES I - VII — EXPERIMENTAL DETAILS OF THE STRUCTURE DETERMINATIONS

APPENDIX VIII — COMPARISONS OF THE PLANARITY AND ASYMMETRY OF THE NITRATE GROUPS IN THE COMPLEXES STUDIED

APPENDIX I

EXPERIMENTAL

BIS[DINITRATOBIS(PYRIDINE)COPPER(II)]-PYRIDINE

Preparation of Crystals

The complex was prepared by the stoicheiometric addition of pyridine to a solution of anhydrous copper nitrate in ethanol. By slow evaporation of a solution of this product in chloroform containing a little pyridine, suitable crystals for an X-ray examination were obtained. Since the crystals slowly decompose in the X-ray beam when in contact with the atmosphere, they were coated in collodion.

Crystal Data

$C_{10}H_{10}N_4O_6Cu$, $0{\cdot}5C_5H_5N$ (monomeric unit)

M = 382.8 (monomer)

Monoclinic

$a = 9.79 \pm 0.03$, $b = 10.89 \pm 0.03$, $c = 16.15 \pm 0.03$ Å,

$\beta = 98.0 \pm 0.2^{\circ}$, $U = 1705$ Å^3

$D_m = 1.50$, $Z = 4$ (for monomer), $D_c = 1.49$

$F(000) = 844$

Space group $P2_1/c$ (C_{2h}^5, No 14) from systematic absences:

$0k0$ for k odd, $h0\ell$ for ℓ odd

Cu-K_α X-rays, $\lambda = 1.5418$ Å

μ(Cu-K_α) = 22.5 cm^{-1}

Crystallographic Measurements

The unit cell parameters were determined from oscillation and Weissenberg photographs taken with Cu-K_α radiation and from precession photographs taken with Mo-K_α (λ = 0.7107 Å) radiation.

A small crystal selected for measurement was rotated about b and 2386 independent reflections from the reciprocal lattice nets h0-9ℓ were recorded on equatorial and equi-inclination Weissenberg photographs by the multiple film technique. The intensities were estimated visually by comparison with a calibrated strip, and corrections for Lorentz, polarisation, and rotation factors made. The calculated structure factors were placed on an overall scale by comparison with those obtained from the 0kℓ reciprocal-lattice net recorded by precession methods. Unobserved reflections were not included in the calculations and absorption corrections were not applied.

Structure Determination and Refinement

The entire structure was determined by conventional Patterson and electron-density calculations with initial phasing appropriate to the copper atom. Several cycles of structure-factor and electron-density calculations effected preliminary refinement and reduced R to 0.23. During these preliminary calculations an overall isotropic vibration parameter, U_{iso} (0.05 Å^2), was assigned to the atoms.

The least-squares refinement of positional, thermal and scale parameters converged after 12 cycles, when R was 0.104 and R' ($= \sum w\Delta^2 / \sum wF_o^2$) was 0.018. Details of the refinement are given in Table 1. After cycle 5 the data were placed on an overall absolute scale and in all subsequent cycles the overall scale parameter was refined.

The refinement of anisotropic thermal parameters after cycle 7 necessitated the use of the block-diagonal approximation to the normal-equation matrix because of computer-store limitations.

In all refinement cycles, the weighting scheme given as equation (32) (Section I.1.8(b)) was applied to the data. Initially the p parameters were chosen to give unit weight to all reflections, but they were varied in later cycles as indicated by a $|F_o|$ and ($\sin\theta/\lambda$) analysis of $\sum w\Delta^2$. The final values are p_1 200, p_2 0.01, p_3 0.0005, and p_4 0.

At the conclusion of the refinement a difference synthesis and final electron-density distribution were evaluated. These calculations revealed no errors in the structure, and although the difference synthesis contained diffuse peaks in positions stereochemically acceptable for hydrogen atoms, it was impossible to determine their coordinates accurately.

In all the structure-factor calculations, the atomic scattering factors used are those given in ref. 212.

The observed and calculated structure factors are listed in Table 2. The fractional coordinates of all non-hydrogen atoms are given in Table 3 and the anisotropic thermal parameters in Table 4.

The relevant interatomic dimensions and some calculated least-squares best planes through the molecule are given in Section II.1.2. The estimated standard deviations recorded were derived from the inverse of the least-squares normal-equation matrix, and are probably best regarded as minimum values.

TABLE 1

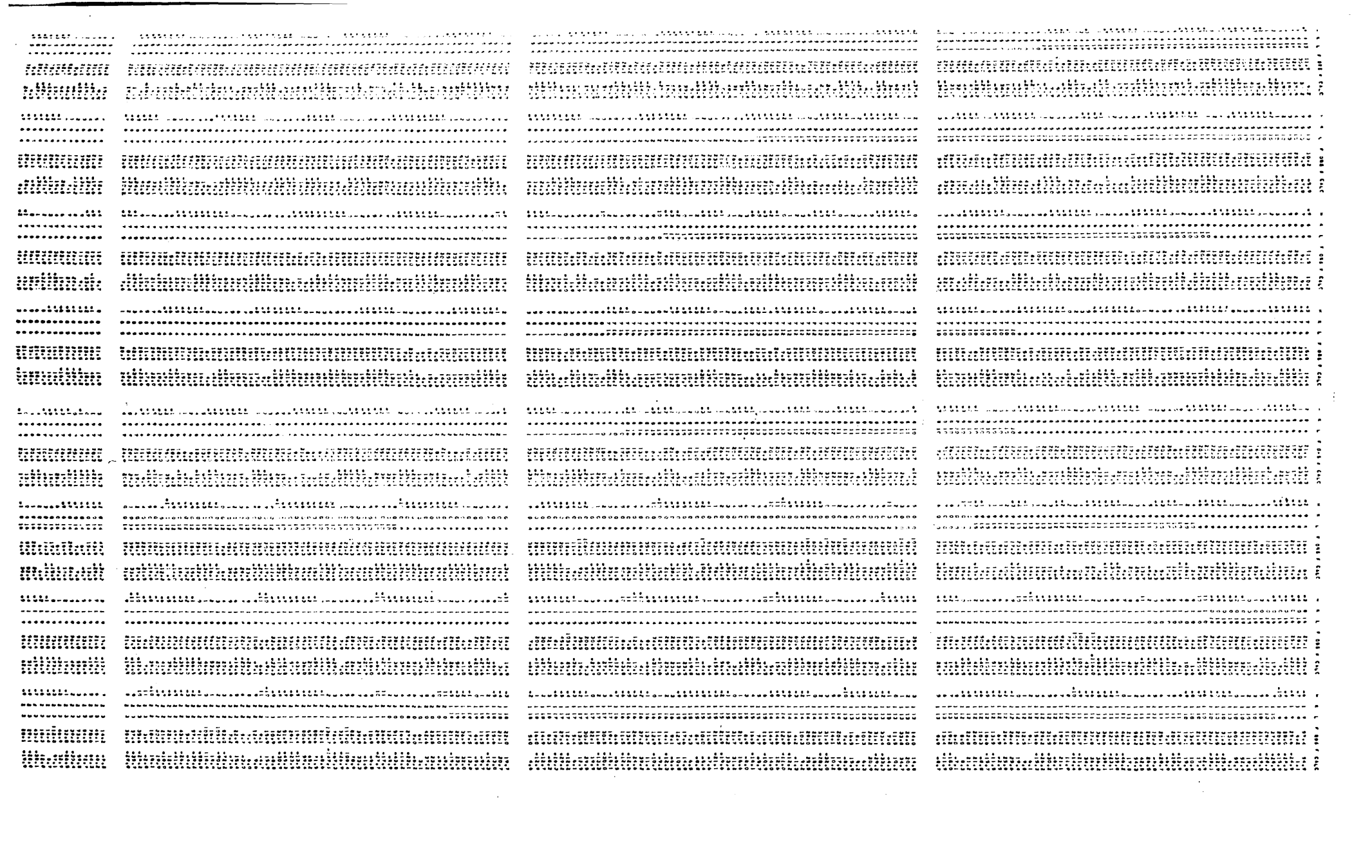
Course of refinement

Cycles	Parameters refined	Final $\underline{R}$	Final $\underline{R'}$
1 - 5	$\underline{x}$, $\underline{y}$, $\underline{z}$, $\underline{U}_{iso}$ for Cu, N, 0, C; layer scale factors $\underline{k}_k$, unit weights, full matrix	0.137	0.0298
6 - 7	$\underline{x}$, $\underline{y}$, $\underline{z}$, $\underline{U}_{iso}$ for Cu, N, 0, C; one overall scale factor. Weighting scheme adjusted, full matrix	0.133	0.0278
8 - 12	$\underline{x}$, $\underline{y}$, $\underline{z}$, $\underline{U}_{ij}$ ($\underline{i}$, $\underline{j}$ = 1, 2, 3) for Cu, N, 0, C. Small adjustments to weighting scheme. Block diagonal approximation to normal equation matrix	0.104	0.0183

TABLE 2

$[Cu(py)_2(NO_3)_2]_2py$

Observed and final-calculated structure amplitudes



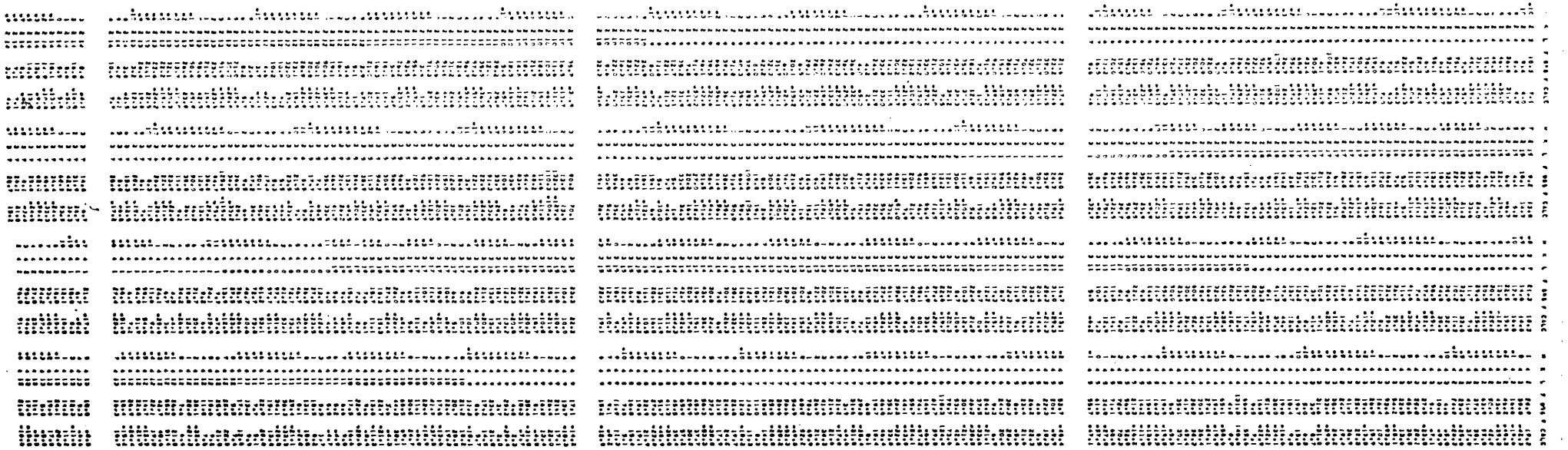


TABLE 3

$[Cu(py)_2(NO_3)_2]_2 \cdot py$

Atom positions (fractional coordinates)

	x/a	y/b	z/c
C(1)	-0.0938(10)	0.2957(10)	0.0082(6)
C(2)	-0.1568(13)	0.3883(11)	-0.0417(8)
C(3)	-0.0945(13)	0.4410(13)	-0.1005(9)
C(4)	0.0386(15)	0.3909(11)	-0.1191(7)
C(5)	0.0969(10)	0.2978(9)	-0.0688(6)
C(6)	0.1402(10)	-0.0942(10)	0.1839(5)
C(7)	0.2020(11)	-0.1877(10)	0.2343(6)
C(8)	0.3450(12)	-0.2082(12)	0.2364(7)
C(9)	0.4245(11)	-0.1378(11)	0.1879(7)
C(10)	0.3556(9)	-0.0481(10)	0.1375(5)
C(11)	0.4970(16)	0.5658(23)	-0.0689(13)
C(12)	0.4595(17)	0.4529(24)	-0.0766(14)
C(13)	0.4649(18)	0.3779(21)	-0.0081(21)
O(1)	0.0801(6)	0.1961(6)	0.1693(4)
O(2)	0.2957(8)	0.2459(9)	0.1563(5)
O(3)	0.1971(10)	0.3158(9)	0.2606(5)
O(4)	0.1145(6)	0.0023(6)	-0.0412(3)
O(5)	0.3280(7)	0.0731(7)	-0.0441(4)
O(6)	0.2460(10)	-0.0720(8)	-0.1293(5)
N(1)	0.1969(8)	0.2530(7)	0.1982(4)
N(2)	0.2366(8)	0.0016(7)	-0.0729(4)
N(3)	0.0316(7)	0.2468(7)	-0.0057(4)
N(4)	0.2148(7)	-0.0243(8)	0.1352(4)
Cu(1)	0.11665(11)	0.10772(11)	0.06356(6)

TABLE 4

$[Cu(py)_2(NO_3)_2]_2.py$

(a) Anisotropic temperature factors ($Å^2$) *

	U_{11}	U_{22}	U_{33}	$2U_{32}$	$2U_{31}$	$2U_{12}$
C(1)	0.041	0.028	0.050	0.020	0.009	-0.009
C(2)	0.057	0.023	0.080	-0.028	-0.035	0.038
C(3)	0.056	0.045	0.091	0.031	-0.068	0.017
C(4)	0.093	0.026	0.049	-0.006	0.003	0.009
C(5)	0.041	0.015	0.040	-0.003	0.000	0.007
C(6)	0.038	0.038	0.025	0.002	-0.002	-0.016
C(7)	0.056	0.028	0.036	0.017	-0.002	-0.020
C(8)	0.058	0.055	0.040	0.023	-0.011	0.006
C(9)	0.040	0.050	0.049	0.026	-0.002	0.041
C(10)	0.021	0.053	0.031	0.015	-0.006	0.013
C(11)	0.049	0.180	0.133	0.187	0.016	0.028
C(12)	0.054	0.155	0.135	0.019	-0.042	-0.017
C(13)	0.047	0.094	0.304	-0.043	0.026	0.029
O(1)	0.034	0.034	0.031	-0.020	0.005	-0.001
O(2)	0.049	0.061	0.063	-0.026	0.046	-0.058
O(3)	0.082	0.069	0.045	-0.061	0.009	-0.042
O(4)	0.024	0.020	0.027	0.005	0.009	0.001
O(5)	0.028	0.041	0.050	-0.010	0.015	0.007
O(6)	0.082	0.052	0.063	0.045	0.084	-0.001
N(1)	0.046	0.018	0.028	-0.017	0.004	-0.015
N(2)	0.033	0.028	0.027	0.005	0.026	-0.003
N(3)	0.029	0.021	0.027	0.006	-0.008	-0.010
N(4)	0.028	0.031	0.020	0.002	0.002	-0.006
Cu(1)	0.032	0.028	0.027	-0.005	0.001	0.001

(b) Average estimated standard deviations ($Å^2$)

C	0.007	0.010	0.010	0.014	0.012	0.012
O	0.004	0.006	0.004	0.007	0.006	0.007
N	0.004	0.005	0.003	0.006	0.005	0.006
Cu	0.001	0.001	0.001	0.001	0.001	0.001

* These are the values of U_{ij} in equation (5) (Section I.1.4(b)).

APPENDIX II

EXPERIMENTAL

DINITRATOBIS(PYRIDINE)-ZINC(II)

Preparation of Crystals

Zinc(II) nitrate hexahydrate was dehydrated by heating under reflux in 2,2-dimethoxypropane for an hour. To this was added a stoicheiometric quantity of pyridine and the resulting complex was recrystallised from ethanol-2,2-dimethoxypropane containing a little pyridine. To prevent decomposition of air-exposed crystals in the X-ray beam, the crystals used in the analysis were coated with collodion.

Crystal Data

$C_{10}H_{10}N_4O_6Zn$

M = 347.4

Monoclinic

$a = 10.27 \pm 0.03$, $b = 18.93 \pm 0.03$, $c = 16.15 \pm 0.03$ Å,

$\beta = 122.8 \pm 0.2^{\circ}$, $U = 1484$ Å^3

$D_m = 1.53$, $Z = 4$, $D_c = 1.55$

F(000) = 704

Space group $P2_1/n$ (equivalent positions, x, y, z; 1/2 + x, 1/2 -y, 1/2 + z; -x, -y, -z; 1/2 - x, 1/2 + y, 1/2 - z)

Cu-K_α X-rays, λ = 1.5418 Å

μ(Cu-K_α) = 26.8 cm^{-1}

Crystallographic Measurements

The unit-cell parameters were determined from oscillation and Weissenberg photographs taken with Cu-K_α radiation, and from precession photographs taken with Mo-K_α (λ = 0.7107 Å) radiation. The systematic absences (0k0 when k is odd, h0ℓ when h + ℓ is odd) uniquely determine the space group as $P2_1/n$.

1044 independent reflections from the reciprocal-lattice nets 0-6kℓ were recorded on equatorial and equi-inclination Weissenberg photographs by the multiple-film technique and were estimated visually by comparison with a calibrated strip. After correction for Lorentz, polarisation, and rotation factors, the structure amplitudes were placed on an overall scale by comparison with values obtained from the h0ℓ reciprocal-lattice net recorded by precession methods. Unobserved reflexions were not included in the calculations and absorption corrections were not applied.

Structure Determination

The position of the zinc atom was determined from the three-dimensional Patterson synthesis, and the other 20 non-hydrogen atom positions were revealed in the first heavy-atom-phased electron-density distribution.

Several cycles of structure-factor and electron-density calculations effected preliminary refinement and reduced R to 0.25. During these calculations, an overall isotropic vibration parameter, U_{iso} (0.06 $\AA^2$), was assigned to all atoms, and the data were placed on an approximate absolute scale by comparison of $k\Sigma|F_o|$ and $\Sigma|F_c|$ for each layer.

Structure Refinement

The least-squares refinement of positional, thermal, and scale parameters converged after 11 cycles when R was 0.100 and R' was 0.018. Details of the refinement are given in Table 5. After cycle 6, the data were placed on an overall absolute scale and in all subsequent cycles the overall scale parameter was refined.

The refinement of anisotropic thermal parameters after cycle 6 necessitated the use of the block-diagonal approximation to the normal-equation matrix because of computer-store limitations.

In all refinement cycles, the weighting scheme given as equation (32) (Section I.1.8(b)) was applied to the data. Initially the parameters, p, were chosen to give unit weights to all reflections, but were varied in later cycles as indicated by a $|F_o|$ and $(\sin\theta/\lambda)$ analysis of $\Sigma w\Delta^2$. The final values are p_1 50, p_2 0.01, p_3 0.001 and p_4 0.

A difference synthesis and a final electron-density distribution calculated at the end of the refinement revealed no errors in the structure. Although there were diffuse peaks in positions stereochemically acceptable for hydrogen atoms, their coordinates could not be determined with any accuracy, and they were not included in the calculations.

In all the previous structure-factor calculations, the atomic scattering factors were taken from ref. 212. The observed and calculated structure factors are listed in Table 6. The fractional coordinates of all non-hydrogen atoms are given in Table 7 and the anisotropic thermal parameters in Table 8.

The relevant interatomic dimensions and some calculated least-squares best planes through the molecule are given in Section II.1.4. The estimated standard deviations recorded were derived from the inverse of the least-squares normal-equation matrix, and are probably best regarded as minimum values.

TABLE 5

Course of refinement

Cycles	Parameters refined	Final $\underline{R}$	Final $\underline{R}'$
1 - 4	$\underline{x}$, $\underline{y}$, $\underline{z}$, $\underline{U}_{iso}$ for Zn, N, 0, C; layer scale factors $\underline{k}_k$, unit weights, full matrix	0.140	0.0352
5 - 6	$\underline{x}$, $\underline{y}$, $\underline{z}$, $\underline{U}_{iso}$ for Zn, N, 0, C; layer scale factors, weighting scheme adjusted, full matrix	0.136	0.0301
7 - 11	$\underline{x}$, $\underline{y}$, $\underline{z}$, $\underline{U}_{ij}$ ($\underline{i}$, $\underline{j}$ = 1, 2, 3) for Zn, N, 0, C. Small adjustments to weighting scheme. Block diagonal approximation to normal equation matrix	0.100	0.0182

TABLE 6

$Zn(py)_2(NO_3)_2$

Observed and final-calculated structure amplitudes

H	K	L	F OBS	F CALC
0	0	4	16.4	15.5
0	0	5	93.1	95.4
0	0	6	5.4	6.6
0	0	7	26.1	-25.1
0	0	8	26.6	-26.0
0	0	9	26.7	-25.4
0	0	10	38.0	-39.7
0	0	11	47.2	-43.4
0	0	12	62.0	-59.9
0	0	13	47.5	46.0
0	0	14	22.1	22.4
0	0	15	42.7	40.7
0	0	16	80.0	75.4
0	0	17	19.7	-19.5
0	0	18	13.7	9.5
0	0	19	91.2	-88.0
0	0	20	24.1	20.9
0	0	21	9.5	-5.6
0	0	22	8.8	-10.2
0	1	1	17.9	17.9
0	1	2	46.5	-49.8
0	1	3	72.5	77.0
0	1	4	32.0	29.9
0	1	5	19.7	-19.5
0	1	6	13.7	9.5
0	1	7	91.2	-88.0
0	1	8	24.1	20.9
0	1	9	9.5	-5.6
0	1	10	8.8	-10.2
0	1	11	17.9	17.9
0	1	12	46.5	-49.8
0	1	13	72.5	77.0
0	1	14	32.0	29.9
0	1	15	19.7	-19.5
0	1	16	13.7	9.5
0	1	17	91.2	-88.0
0	1	18	24.1	20.9
0	1	19	9.5	-5.6
0	1	20	8.8	-10.2
0	2	2	17.9	17.9
0	2	3	46.5	-49.8
0	2	4	72.5	77.0
0	2	5	32.0	29.9
0	2	6	19.7	-19.5
0	2	7	13.7	9.5
0	2	8	91.2	-88.0
0	2	9	24.1	20.9
0	2	10	9.5	-5.6
0	2	11	8.8	-10.2
0	2	12	17.9	17.9
0	2	13	46.5	-49.8
0	2	14	72.5	77.0
0	2	15	32.0	29.9
0	2	16	19.7	-19.5
0	2	17	13.7	9.5
0	2	18	91.2	-88.0
0	2	19	24.1	20.9
0	2	20	9.5	-5.6
0	3	3	17.9	17.9
0	3	4	46.5	-49.8
0	3	5	72.5	77.0
0	3	6	32.0	29.9
0	3	7	19.7	-19.5
0	3	8	13.7	9.5
0	3	9	91.2	-88.0
0	3	10	24.1	20.9
0	3	11	9.5	-5.6
0	3	12	8.8	-10.2
0	3	13	17.9	17.9
0	3	14	46.5	-49.8
0	3	15	72.5	77.0
0	3	16	32.0	29.9
0	3	17	19.7	-19.5
0	3	18	13.7	9.5
0	3	19	91.2	-88.0
0	3	20	24.1	20.9
0	4	4	17.9	17.9
0	4	5	46.5	-49.8
0	4	6	72.5	77.0
0	4	7	32.0	29.9
0	4	8	19.7	-19.5
0	4	9	13.7	9.5
0	4	10	91.2	-88.0
0	4	11	24.1	20.9
0	4	12	9.5	-5.6
0	4	13	8.8	-10.2
0	4	14	17.9	17.9
0	4	15	46.5	-49.8
0	4	16	72.5	77.0
0	4	17	32.0	29.9
0	4	18	19.7	-19.5
0	4	19	13.7	9.5
0	4	20	91.2	-88.0
0	5	5	24.1	20.9
0	5	6	9.5	-5.6
0	5	7	8.8	-10.2
0	5	8	17.9	17.9
0	5	9	46.5	-49.8
0	5	10	72.5	77.0
0	5	11	32.0	29.9
0	5	12	19.7	-19.5
0	5	13	13.7	9.5
0	5	14	91.2	-88.0
0	5	15	24.1	20.9
0	5	16	9.5	-5.6
0	5	17	8.8	-10.2
0	5	18	17.9	17.9
0	5	19	46.5	-49.8
0	5	20	72.5	77.0
0	6	6	32.0	29.9
0	6	7	19.7	-19.5
0	6	8	13.7	9.5
0	6	9	91.2	-88.0
0	6	10	24.1	20.9
0	6	11	9.5	-5.6
0	6	12	8.8	-10.2
0	6	13	17.9	17.9
0	6	14	46.5	-49.8
0	6	15	72.5	77.0
0	6	16	32.0	29.9
0	6	17	19.7	-19.5
0	6	18	13.7	9.5
0	6	19	91.2	-88.0
0	6	20	24.1	20.9
0	7	7	9.5	-5.6
0	7	8	8.8	-10.2
0	7	9	17.9	17.9
0	7	10	46.5	-49.8
0	7	11	72.5	77.0
0	7	12	32.0	29.9
0	7	13	19.7	-19.5
0	7	14	13.7	9.5
0	7	15	91.2	-88.0
0	7	16	24.1	20.9
0	7	17	9.5	-5.6
0	7	18	8.8	-10.2
0	7	19	17.9	17.9
0	7	20	46.5	-49.8
0	8	8	72.5	77.0
0	8	9	32.0	29.9
0	8	10	19.7	-19.5
0	8	11	13.7	9.5
0	8	12	91.2	-88.0
0	8	13	24.1	20.9
0	8	14	9.5	-5.6
0	8	15	8.8	-10.2
0	8	16	17.9	17.9
0	8	17	46.5	-49.8
0	8	18	72.5	77.0
0	8	19	32.0	29.9
0	8	20	19.7	-19.5
0	9	9	13.7	9.5
0	9	10	91.2	-88.0
0	9	11	24.1	20.9
0	9	12	9.5	-5.6
0	9	13	8.8	-10.2
0	9	14	17.9	17.9
0	9	15	46.5	-49.8
0	9	16	72.5	77.0
0	9	17	32.0	29.9
0	9	18	19.7	-19.5
0	9	19	13.7	9.5
0	9	20	91.2	-88.0
0	10	10	24.1	20.9
0	10	11	9.5	-5.6
0	10	12	8.8	-10.2
0	10	13	17.9	17.9
0	10	14	46.5	-49.8
0	10	15	72.5	77.0
0	10	16	32.0	29.9
0	10	17	19.7	-19.5
0	10	18	13.7	9.5
0	10	19	91.2	-88.0
0	10	20	24.1	20.9
0	11	11	9.5	-5.6
0	11	12	8.8	-10.2
0	11	13	17.9	17.9
0	11	14	46.5	-49.8
0	11	15	72.5	77.0
0	11	16	32.0	29.9
0	11	17	19.7	-19.5
0	11	18	13.7	9.5
0	11	19	91.2	-88.0
0	11	20	24.1	20.9
0	12	12	9.5	-5.6
0	12	13	8.8	-10.2
0	12	14	17.9	17.9
0	12	15	46.5	-49.8
0	12	16	72.5	77.0
0	12	17	32.0	29.9
0	12	18	19.7	-19.5
0	12	19	13.7	9.5
0	12	20	91.2	-88.0
0	13	13	24.1	20.9
0	13	14	9.5	-5.6
0	13	15	8.8	-10.2
0	13	16	17.9	17.9
0	13	17	46.5	-49.8
0	13	18	72.5	77.0
0	13	19	32.0	29.9
0	13	20	19.7	-19.5
0	14	14	13.7	9.5
0	14	15	91.2	-88.0
0	14	16	24.1	20.9
0	14	17	9.5	-5.6
0	14	18	8.8	-10.2
0	14	19	17.9	17.9
0	14	20	46.5	-49.8
0	15	15	72.5	77.0
0	15	16	32.0	29.9
0	15	17	19.7	-19.5
0	15	18	13.7	9.5
0	15	19	91.2	-88.0
0	15	20	24.1	20.9
0	16	16	9.5	-5.6
0	16	17	8.8	-10.2
0	16	18	17.9	17.9
0	16	19	46.5	-49.8
0	16	20	72.5	77.0
0	17	17	32.0	29.9
0	17	18	19.7	-19.5
0	17	19	13.7	9.5
0	17	20	91.2	-88.0
0	18	18	24.1	20.9
0	18	19	9.5	-5.6
0	18	20	8.8	-10.2
0	19	19	17.9	17.9
0	19	20	46.5	-49.8
0	20	20	72.5	77.0
1	0	1	7.5	-8.4
1	0	2	13.4	-13.2
1	0	3	6.2	9.0
1	0	4	12.3	13.6
1	0	5	37.2	35.8
1	0	6	37.6	39.6
1	0	7	37.6	-37.7
1	0	8	43.9	-46.0
1	0	9	49.5	47.0
1	0	10	13.0	-10.7
1	0	11	17.8	16.4
1	0	12	47.4	44.8
1	0	13	38.4	-33.6
1	0	14	55.6	59.2
1	0	15	19.9	-19.0
1	0	16	21.1	-20.2
1	0	17	39.4	40.7
1	0	18	10.3	-9.2
1	0	19	22.6	-22.1
1	0	20	15.6	16.1
1	1	1	39.2	-40.6
1	1	2	26.1	27.7
1	1	3	27.3	-27.2
1	1	4	22.1	22.6
1	1	5	9.1	-10.6
1	1	6	99.3	97.5
1	1	7	7.4	7.2
1	1	8	95.8	93.2
1	1	9	98.1	-93.1
1	1	10	47.1	45.4
1	1	11	92.1	-46.7
1	1	12	60.5	-56.4
1	1	13	19.2	-18.2
1	1	14	20.5	20.2
1	1	15	10.4	-12.7
1	1	16	80.7	-21.4
1	1	17	15.0	12.8
1	1	18	40.5	34.4
1	1	19	44.2	-44.8
1	1	20	44.2	38.4
1	2	0	14.1	-14.1
1	2	1	84.2	73.2
1	2	2	26.3	-28.6
1	2	3	34.7	36.8
1	2	4	11.4	-12.7
1	2	5	20.4	20.7
1	2	6	19.2	-18.2
1	2	7	27.2	27.2
1	2	8	20.5	-19.2
1	2	9	80.7	24.3
1	2	10	11.5	8.7
1	2	11	32.0	-29.4
1	2	12	13.4	13.7
1	2	13	27.8	-24.9
1	2	14	16.0	-14.9
1	2	15	93.1	-87.9
1	2	16	63.1	-61.0
1	2	17	49.8	-45.5
1	2	18	44.6	38.6
1	2	19	65.3	-70.6
1	2	20	19.4	16.3
1	3	3	19.9	-21.4
1	3	4	8.0	-9.0
1	3	5	81.1	77.8
1	3	6	46.9	35.2
1	3	7	13.6	13.4
1	3	8	10.2	-9.0
1	3	9	60.1	58.6
1	3	10	21.6	22.3
1	3	11	19.2	19.2
1	3	12	44.6	46.0
1	3	13	6.8	-4.1
1	3	14	12.6	-12.7
1	3	15	20.6	-19.2
1	3	16	13.6	13.7
1	3	17	17.6	18.6
1	3	18	40.4	-36.1
1	3	19	22.1	17.8
1	3	20	6.4	6.3
1	4	4	32.0	-29.4
1	4	5	19.4	16.3
1	4	6	19.9	-21.4
1	4	7	8.0	-9.0
1	4	8	27.6	-24.9
1	4	9	16.0	-14.9
1	4	10	93.1	-87.9
1	4	11	63.1	-61.0
1	4	12	49.8	-45.5
1	4	13	44.6	38.6
1	4	14	65.3	-70.6
1	4	15	19.4	16.3
1	4	16	19.9	-21.4
1	4	17	8.0	-9.0
1	4	18	27.6	-24.9
1	4	19	16.0	-14.9
1	4	20	93.1	-87.9
1	5	5	63.1	-61.0
1	5	6	49.8	-45.5
1	5	7	44.6	38.6
1	5	8	65.3	-70.6
1	5	9	19.4	16.3
1	5	10	19.9	-21.4
1	5	11	8.0	-9.0
1	5	12	27.6	-24.9
1	5	13	16.0	-14.9
1	5	14	93.1	-87.9
1	5	15	63.1	-61.0
1	5	16	49.8	-45.5
1	5	17	44.6	38.6
1	5	18	65.3	-70.6
1	5	19	19.4	16.3
1	5	20	19.9	-21.4
1	6	6	8.0	-9.0
1	6	7	27.6	-24.9
1	6	8	16.0	-14.9
1	6	9	93.1	-87.9
1	6	10	63.1	-61.0
1	6	11	49.8	-45.5
1	6	12	44.6	38.6
1	6	13	65.3	-70.6
1	6	14	19.4	16.3
1	6	15	19.9	-21.4
1	6	16	8.0	-9.0
1	6	17	27.6	-24.9
1	6	18	16.0	-14.9
1	6	19	93.1	-87.9
1	6	20	63.1	-61.0
1	7	7	49.8	-45.5
1	7	8	44.6	38.6
1	7	9	65.3	-70.6
1	7	10	19.4	16.3
1	7	11	19.9	-21.4
1	7	12	8.0	-9.0
1	7	13	27.6	-24.9
1	7	14	16.0	-14.9
1	7	15	93.1	-87.9
1	7	16	63.1	-61.0
1	7	17	49.8	-45.5
1	7	18	44.6	38.6
1	7	19	65.3	-70.6
1	7	20	19.4	16.3
1	8	8	19.9	-21.4
1	8	9	8.0	-9.0
1	8	10	27.6	-24.9
1	8	11	16.0	-14.9
1	8	12	93.1	-87.9
1	8	13	63.1	-61.0
1	8	14	49.8	-45.5
1	8	15	44.6	38.6
1	8	16	65.3	-70.6
1	8	17	19.4	16.3
1	8	18	19.9	-21.4
1	8	19	8.0	-9.0
1	8	20	27.6	-24.9
1	9	9	16.0	-14.9
1	9	10	93.1	-87.9
1	9	11	63.1	-61.0
1	9	12	49.8	-45.5
1	9	13	44.6	38.6
1	9	14	65.3	-70.6
1	9	15	19.4	16.3
1	9	16	19.9	-21.4
1	9	17	8.0	-9.0
1	9	18	27.6	-24.9
1	9	19	16.0	-14.9
1	9	20	93.1	-87.9
1	10	10	63.1	-61.0
1	10	11	49.8	-45.5
1	10	12	44.6	38.6
1	10	13	65.3	-70.6
1	10	14	19.4	16.3
1	10	15	19.9	-21.4
1	10	16	8.0	-9.0
1	10	17	27.6	-24.9
1	10	18	16.0	-14.9
1	10	19	93.1	-87.9
1	10	20	63.1	-61.0
1	11	11	49.8	-45.5
1	11	12	44.6	38.6
1	11	13	65.3	-70.6
1	11	14	19.4	16.3
1	11	15	19.9	-21.4
1	11	16	8.0	-9.0
1	11	17	27.6	-24.9
1	11	18	16.0	-14.9
1	11	19	93.1	-87.9
1	11	20	63.1	-61.0
1	12	12	49.8	-45.5
1	12	13	44.6	38.6
1	12	14	65.3	-70.6
1	12	15	19.4	16.3
1	12	16	19.9	-21.4
1	12	17	8.0	-9.0
1	12	18	27.6	-24.9
1	12	19	16.0	-14.9
1	12	20	93.1	-87.9
1	13	13	63.1	-61.0
1	13	14	49.8	-45.5
1	13	15	44.6	38.6
1	13	16	65.3	-70.6
1	13	17	19.4	16.3
1	13	18	19.9	-21.4
1	13	19	8.0	-9.0
1	13	20	27.6	-24.9
1	14	14	16.0	-14.9
1	14	15	93.1	-87.9
1	14	16	63.1	-61.0
1	14	17	49.8	-45.5
1	14	18	44.6	38.6
1	14	19	65.3	-70.6
1	14	20	19.4	16.3
1	15	15	19.9	-21.4
1	15	16	8.0	-9.0
1	15	17	27.6	-24.9
1	15	18	16.0	-14.9
1	15	19	93.1	-87.9
1	15	20	63.1	-61.0
1	16	16	49.8	-45.5
1	16	17	44.6	38.6
1	16	18	65.3	-70.6
1	16	19	19.4	16.3
1	16	20	19.9	-21.4
1	17	17	8.0	-9.0
1	17	18	27.6	-24.9
1	17	19	16.0	-14.9
1	17	20	93.1	-87.9
1	18	18	63.1	-61.0
1	18	19	49.8	-45.5
1	18	20	44.6	38.6
1	19	19	65.3	-70.6
1	19	20	19.4	16.3
1	20	20	19.9	-21.4
2	0	2	7.4	-7.7
2	0	3	96.4	-93.3
2	0	4	95.8	-92.7
2	0	5	47.9	-47.0
2	0	6	67.4	-72.8
2	0	7	24.1	-22.9
2	0	8	28.8	-31.9
2	0	9	17.4	16.9
2	0	10	39.2	39.4
2	0	11	11.0	-12.9
2	0	12	32.4	33.7
2	0	13	19.5	19.6
2	0	14	6.8	7.7
2	0	15	7.1	6.6
2	1	1	96.4	-93.3
2	1	2	95.8	-92.7
2	1	3	47.9	-47.0
2	1	4	67.4	-72.8
2	1	5	24.1	-22.9
2	1	6	28.8	-31.9
2	1	7	17.4	16.9
2	1	8	39.2	39.4
2	1	9	11.0	-12.9
2	1	10	32.4	33.7
2	1	11	19.5	19.6
2	1	12	6.8	7.7
2	1	13	7.1	6.6
2	2	2	47.9	-47.0
2	2	3	67.4	-72.8
2	2	4	24.1	-22.9
2	2	5	28.8	-31.9
2	2	6	17.4	16.9
2	2	7	39.2	39.4
2	2	8	11.0	-12.9
2	2	9	32.4	33.7
2	2	10	19.5	19.6
2	2	11	6.8	7.7
2	2	12	7.1	6.6
2	3	3	24.1	-22.9
2	3	4	28.8	-31.9
2	3	5	17.4	16.9
2	3	6	39.2	39.4
2	3	7	11.0	-12.9
2	3	8	32.4	33.7
2	3	9	19.5	19.6
2	3	10	6.8	7.7
2	3	11	7.1	6.6
2	4	4	47.9	-47.0
2	4	5	67.4	-72.8
2	4	6	24.1	-22.9
2	4	7	28.8	-31.9
2	4	8	17.4	16.9
2	4	9	39.2	39.4
2	4	10	11.0	-12.9
2	4	11	32.4	33.7
2	4	12	19.5	19.6
2	4	13	6.8	7.7
2	4	14	7.1	6.6
2	5	5	24.1	-22.9
2	5	6	28.8	-31.9
2	5	7	17.4	16.9
2	5	8	39.2	39.4
2	5	9	11.0	-12.9
2	5	10	32.4	33.7
2	5	11	19.5	19.6
2	5	12	6.8	7.7
2	5	13	7.1	6.6
2	6	6	47.9	-47.0
2	6	7	67.4	-72.8
2	6	8	24.1	-22.9
2	6	9	28.8	-31.9
2	6	10	17.4	16.9
2	6	11	39.2	39.4
2	6	12	11.0	-12.9
2	6	13	32.4	33.7
2	6	14	19.5	19.6
2	6	15	6.8	7.7
2	6	16	7.1	6.6
2	7	7	24.1	-22.9
2	7	8	28.8	-31.9
2	7	9	17.4	16.9
2	7	10	39.2	39.4
2	7	11	11.0	-12.9
2	7	12	32.4	33.7
2	7	13	19.5	19.6
2	7	14	6.8	7.7
2	7	15	7.1	6.6
2	8	8	47.9	-47.0
2	8	9	67.4	-72.8
2	8	10	24.1	-22.9
2	8	11	28.8	-31.9
2	8	12	17.4	16.9
2	8	13	39.2	39.4
2	8	14	11.0	-12.9
2	8	15	32.4	33.7
2	8	16	19.5	19.6
2	8	17	6.8	7.7
2	8	18	7.1	6.6
2	9	9	24.1	-22.9
2	9	10	28.8	-31.9
2	9	11	17.4	16.9
2	9	12	39.2	39.4
2	9	13	11.0	-12.9
2	9	14	32.4	33.7
2	9	15	19.5	19.6
2	9	16	6.8	7.7
2	9	17	7.1	6.6
2	10	10	47.9	-47.0
2	10	11	67.4	-72.8
2	10	12	24.1	-22.9
2	10	13	28.8	-31.9
2	10	14	17.4	16.9
2	10	15	39.2	39.4
2	10	16	11.0	-12.9
2	10	17	32.4	33.7
2	10	18	19.5	19.6
2	10	19	6.8	7.7
2	10	20	7.1	6.6
2	11	11	24.1	-22.9
2	11	12	28.8	-31.9
2	11	13	17.4	16.9
2	11	14	39.2	39.4
2	11	15	11.0	-12.9
2	11	16	32.4	33.7
2	11	17	19.5	19.6
2	11	18	6.8	7.7
2	11	19	7.1	6.6
2	12	12	47.9	-47.0
2	12	13	67.4	-72.8
2	12	14	24.1	-22.9
2	12	15	28.8	-31.9
2	12	16	17.4	16.9
2	12	17	39.2	39.4
2	12	18	11.0	-12.9
2	12	19	32.4	33.7
2	12	20	19.5	19.6
2	13	13	24.1	-22.9
2	13	14	28.8	-31.9
2	13	15	17.4	16.9
2	13	16	39.2	39.4
2	13	17	11.0	-12.9
2	13	18	32.4	33.7
2	13	19	19.5	19.6
2	13	20	6.8	7.7
2	14	14	24.1	-22.9
2	14	15	28.8	-31.9
2	14	16	17.4	16.9
2	14	17	39.2	39.4
2	14	18	11.0	-12.9
2	14	19	32.4	33.7
2	14	20	19.5	19.6
2	15	15	24.1	-22.9
2	15	16	28.8	-

TABLE 7

$Zn(py)_2(NO_3)_2$

Atom positions (fractional coordinates)

	x/a	y/b	z/c
Zn(1)	0.27964(26)	0.13448(10)	0.46821(23)
C(1)	0.0708(24)	0.1203(9)	0.0806(21)
C(2)	0.0261(24)	0.0934(11)	-0.0881(21)
C(3)	0.1185(25)	0.0456(10)	-0.1068(20)
C(4)	0.2574(22)	0.0220(9)	0.0399(20)
C(5)	0.2936(20)	0.0488(9)	0.2068(19)
C(6)	0.1336(22)	0.2644(8)	0.5122(21)
C(7)	0.0260(26)	0.3032(9)	0.5308(25)
C(8)	-0.1000(25)	0.2691(9)	0.5157(22)
C(9)	-0.1240(23)	0.1930(9)	0.4711(23)
C(10)	-0.0101(23)	0.1578(8)	0.4626(19)
O(1)	0.5780(22)	0.1261(9)	0.5440(23)
O(2)	0.4502(14)	0.2090(6)	0.5857(14)
O(3)	0.7024(17)	0.2203(7)	0.7025(18)
O(4)	0.3865(16)	0.0612(6)	0.6650(16)
O(5)	0.1654(19)	0.0078(7)	0.5008(18)
O(6)	0.3335(18)	-0.0412(6)	0.7485(16)
N(1)	0.5777(20)	0.1849(8)	0.6133(19)
N(2)	0.2959(17)	0.0076(6)	0.6407(16)
N(3)	0.2087(17)	0.0973(6)	0.2278(15)
N(4)	0.1147(14)	0.1902(6)	0.4802(13)

TABLE 8

$Zn(py)_2(NO_3)_2$

(a) Anisotropic temperature factors *

	$\underline{U}_{11}$	$\underline{U}_{22}$	$\underline{U}_{33}$	$2\underline{U}_{32}$	$2\underline{U}_{31}$	$2\underline{U}_{12}$
Zn(1)	0.053	0.051	0.041	-0.017	0.062	-0.006
C(1)	0.059	0.058	0.040	0.006	0.064	0.001
C(2)	0.048	0.082	0.044	0.013	0.060	-0.002
C(3)	0.067	0.093	0.026	-0.026	0.070	-0.019
C(4)	0.050	0.070	0.039	-0.043	0.061	0.023
C(5)	0.027	0.063	0.042	-0.024	0.054	-0.006
C(6)	0.066	0.036	0.051	-0.003	0.080	-0.006
C(7)	0.082	0.042	0.071	-0.017	0.097	-0.008
C(8)	0.076	0.057	0.057	-0.018	0.098	0.004
C(9)	0.056	0.048	0.063	-0.024	0.072	0.015
C(10)	0.069	0.037	0.044	0.003	0.080	-0.005
O(1)	0.097	0.092	0.098	-0.091	0.099	-0.060
O(2)	0.053	0.047	0.051	0.015	0.067	0.005
O(3)	0.062	0.081	0.075	-0.051	0.081	-0.032
O(4)	0.060	0.055	0.068	0.007	0.066	-0.016
O(5)	0.072	0.072	0.064	0.020	0.044	-0.016
O(6)	0.099	0.042	0.057	0.016	0.097	-0.001
N(1)	0.066	0.054	0.061	-0.011	0.089	-0.012
N(2)	0.047	0.041	0.044	0.005	0.057	0.005
N(3)	0.050	0.032	0.037	0.002	0.055	0.027
N(4)	0.030	0.035	0.022	-0.007	0.042	-0.007

(b) Average estimated standard deviations (Å^2)

Zn	0.002	0.001	0.001	0.002	0.002	0.002
C	0.014	0.011	0.008	0.014	0.017	0.018
O	0.011	0.007	0.008	0.012	0.013	0.014
N	0.010	0.007	0.006	0.010	0.014	0.012

* These are the values of U_{ij} in equation (5) (Section I.1.4(b)).

APPENDIX III

EXPERIMENTAL

DIAQUO[BISNITRATOBIS(PYRIDINE)]-NICKEL(II)

Preparation of Crystals

Crystals of $Ni(py)_2(NO_3)_2(H_2O)_2$ were prepared from an acetone solution containing stoicheiometric amounts of $Ni(NO_3)_2.2H_2O$ and pyridine. The crystals are blue needles elongated along a. To avoid problems of atmospheric decomposition in the X-ray beam, the crystals were enclosed in a thin-walled glass capillary.

Crystal Data

$C_{10}H_{14}N_4O_8Ni$

M = 358.9

Monoclinic

a = 8.787 ± 0.002, b = 11.725 ± 0.005, c = 7.548 ± 0.002 Å, β = 106.94 ± 0.02°, U = 744 Å^3

D_m = 1.60, Z = 2, D_c = 1.603

F(000) = 388

Space group $P2_1/c$ (C_{2h}^5, No 14) from systematic absences: 0k0 for k odd, h0ℓ for ℓ odd

Mo-K_α X-rays, λ = 0.7107 Å

μ(Mo-K_α) = 14.0 cm^{-1}

Crystallographic Measurements

The unit-cell parameters were initially determined from oscillation and Weissenberg photographs taken with Cu-K_α radiation (λ = 1.5418 Å), and from precession photographs taken with Mo-K_α radiation. These were subsequently adjusted by least-squares refinement of θ, χ, and ϕ setting angles of twelve reflections determined on a Hilger and Watts Y 290 diffractometer.

For the intensity measurements zirconium-filtered molybdenum radiation was used and 2161 reflections were collected by use of the θ to 2θ scan technique. Of these some 1849 reflections were considered observed using the criteria $I \geqslant 1\sigma(I)$, where σ was determined from counter statistics. Values of I were corrected for Lorentz-polarisation effects but no corrections for absorption were made.

Structure Determination and Refinement

Since the density indicated Z=2, and also the data were observed to be systematically weak when $k + \ell = 2n$, it was thought that the nickel atoms would occupy crystallographic special positions. This was confirmed by a three-dimensional Patterson synthesis, and an electron-density calculation with the initial phasing appropriate to the nickel atom revealed all the other non-hydrogen atom

positions. Several cycles of structure-factor and electron-density calculations effected preliminary refinement and reduced R to 0.27. During these preliminary calculations an overall isotropic vibration parameter, U_{iso} (0.05 Å^2), was assigned to the atoms.

The least-squares refinement of positional, thermal, and scale parameters converged after 9 cycles, when R was 0.44 and R' was 0.003. After cycle 5, a difference Fourier synthesis was calculated which revealed positions for all the hydrogen atoms. In subsequent cycles these were refined using isotropic temperature factors (for details of the refinement see Table 9).

In all refinement cycles, the weighting scheme given as equation (32) (Section I.1.8(b)) was applied to the data. Initially the p parameters were chosen to give unit weight to all reflections, but they were varied in later cycles as indicated by a $|F_o|$ and $(\sin\theta/\lambda)$ analysis of $\Sigma w\Delta^2$. The final values are p_1 50, p_2 0.01, p_3 0.001 and p_4 0.

At the conclusion of the refinement a difference synthesis and final electron-density distribution were calculated. These revealed no errors in the structure.

In all the structure-factor calculations, the atomic scattering factors used are those given in ref. 212. The observed and calculated structure factors are listed in Table 10. Fractional coordinates of all non-hydrogen atoms are given in Table 11 and anisotropic thermal

parameters in Table 12. The positions of the hydrogen atoms and their isotropic thermal parameters are given in Table 13.

The relevant interatomic dimensions and some calculated least-squares best planes through the molecule are given in Section II.1.6. The estimated standard deviations recorded were derived from the inverse of the least-squares normal-equation matrix, and are probably best regarded as minimum values.

TABLE 9

Course of refinement

Cycles	Parameters refined	Final $\underline{R}$	Final $\underline{R'}$
1 - 3	$\underline{x}$, $\underline{y}$, $\underline{z}$, $\underline{U_{iso}}$ for Ni, N, 0, C; one overall scale factor $\underline{K_k}$, unit weights, full matrix	0.1003	0.0121
4 - 5	$\underline{x}$, $\underline{y}$, $\underline{z}$, $\underline{U_{iso}}$ for Ni, N, 0, C; one overall scale factor, weighting scheme adjusted, full matrix	0.0934	0.0106
6	$\underline{x}$, $\underline{y}$, $\underline{z}$, $\underline{U_{iso}}$ for Ni, N, 0, C, H; one overall scale factor, weighting scheme adjusted, full matrix	0.0879	0.0094
7 - 9	$\underline{x}$, $\underline{y}$, $\underline{z}$, $\underline{U_{ij}}$ ($\underline{i}$, $\underline{j}$ = 1, 2, 3) for Ni, N, 0, C; $\underline{x}$, $\underline{y}$, $\underline{z}$, $\underline{U_{iso}}$ for H; one overall scale factor, small adjustments to weighting scheme, full matrix	0.0444	0.0030

TABLE 10

$Ni(py)_2(NO_3)_2(H_2O)_2$

Observed and final-calculated structure amplitudes

H	K	L	F OBS	F CALC
12	3	-3	9.4	9.0
12	3	-4	2.6	4.6
12	2	-1	5.4	-3.6
12	2	-2	8.0	7.4
12	2	-3	9.4	9.2
12	2	-4	2.9	3.1
12	1	-1	7.7	7.9
12	1	-2	3.C	-0.2
12	1	-3	3.C	3.4
12	1	-4	4.6	4.6
12	0	-5	5.C	4.7
12	0	-4	5.7	5.9
12	0	-3	5.7	5.1
11	7	-4	3.9	-0.7
11	6	-1	7.6	8.1
11	6	-2	4.2	4.6
11	6	-3	4.7	5.3
11	6	-4	5.7	5.7
11	5	-1	6.6	5.6
11	5	-3	6.0	4.5
11	5	-4	5.7	6.0
11	4	1	3.2	3.5
11	4	0	10.0	9.6
11	4	-1	12.7	10.9
11	4	-2	8.0	7.9
11	4	-3	6.0	6.0
11	4	-4	7.6	6.0
11	3	1	8.6	8.5
11	3	0	3.0	-1.3
11	3	-1	12.4	11.7
11	3	-2	8.6	8.4
11	3	-3	14.6	14.6
11	3	-4	3.6	-3.2
11	2	-1	10.2	10.0
11	2	-2	10.7	10.8
11	2	-3	3.2	2.7
11	2	-4	4.6	4.7
11	1	-1	9.1	8.1
11	1	-2	5.4	5.3
11	1	-3	6.6	6.3
11	1	-4	5.7	5.7
11	0	-5	5.7	5.1
11	0	-4	5.7	5.9
10	8	-1	3.C	-3.1
10	8	-2	3.C	3.4
10	7	-1	11.8	11.3
10	7	-2	5.1	6.1
10	7	-3	7.7	7.3
10	7	-4	5.2	-5.2
10	6	-1	3.6	4.9
10	6	-2	2.6	3.4
10	6	-3	3.C	3.0
10	6	-4	4.6	4.6
10	5	-1	11.8	10.9
10	5	-2	7.9	7.7
10	5	-3	9.4	9.3
10	5	-4	10.7	10.4
10	4	0	3.8	4.0
10	4	-1	11.2	10.2
10	4	-2	12.1	12.3
10	4	-3	6.6	-7.3
10	4	-4	10.7	10.6
10	3	-1	11.6	11.6
10	3	-2	3.7	3.2
10	3	-3	5.8	6.4
10	3	-4	5.6	5.9
10	2	-1	5.6	6.8
10	2	-2	12.9	12.8
10	2	-3	3.6	3.8
10	2	-4	13.2	13.1
10	1	-1	9.6	9.2
10	1	-2	3.C	-3.4
10	1	-3	7.7	-2.7
10	1	-4	7.0	7.0
10	0	-5	12.5	12.5
10	0	-4	4.2	4.1
10	0	-3	12.7	12.5
10	0	-2	11.7	11.8
9	8	-1	3.C	3.4
9	8	-2	3.C	3.4
9	7	-1	11.8	11.6
9	7	-2	5.1	5.1
9	7	-3	7.7	7.9
9	7	-4	5.2	-5.2
9	6	-1	3.6	4.9
9	6	-2	2.6	3.4
9	6	-3	3.C	3.0
9	6	-4	4.6	4.6
9	5	-1	11.8	10.9
9	5	-2	7.9	7.7
9	5	-3	9.4	9.3
9	5	-4	10.7	10.4
9	4	0	3.8	4.0
9	4	-1	11.2	10.2
9	4	-2	12.1	12.3
9	4	-3	6.6	-7.3
9	4	-4	10.7	10.6
9	3	-1	11.6	11.6
9	3	-2	3.7	3.2
9	3	-3	5.8	6.4
9	3	-4	5.6	5.9
9	2	-1	5.6	6.8
9	2	-2	12.9	12.8
9	2	-3	3.6	3.8
9	2	-4	13.2	13.1
9	1	-1	9.6	9.2
9	1	-2	3.C	-3.4
9	1	-3	7.7	-2.7
9	1	-4	7.0	7.0
9	0	-5	12.5	12.5
9	0	-4	4.2	4.1
9	0	-3	12.7	12.5
9	0	-2	11.7	11.8
8	8	-1	3.C	3.4
8	8	-2	3.C	3.4
8	7	-1	15.8	15.8
8	7	-2	5.1	6.1
8	7	-3	7.7	7.3
8	7	-4	5.2	-5.2
8	6	-1	3.6	4.9
8	6	-2	2.6	3.4
8	6	-3	3.C	3.0
8	6	-4	4.6	4.6
8	5	-1	11.8	10.9
8	5	-2	7.9	7.7
8	5	-3	9.4	9.3
8	5	-4	10.7	10.4
8	4	0	3.8	4.0
8	4	-1	11.2	10.2
8	4	-2	12.1	12.3
8	4	-3	6.6	-7.3
8	4	-4	10.7	10.6
8	3	-1	11.6	11.6
8	3	-2	3.7	3.2
8	3	-3	5.8	6.4
8	3	-4	5.6	5.9
8	2	-1	5.6	6.8
8	2	-2	12.9	12.8
8	2	-3	3.6	3.8
8	2	-4	13.2	13.1
8	1	-1	9.6	9.2
8	1	-2	3.C	-3.4
8	1	-3	7.7	-2.7
8	1	-4	7.0	7.0
8	0	-5	12.5	12.5
8	0	-4	4.2	4.1
8	0	-3	12.7	12.5
8	0	-2	11.7	11.8
7	8	-1	3.C	3.4
7	8	-2	3.C	3.4
7	7	-1	15.8	15.8
7	7	-2	5.1	6.1
7	7	-3	7.7	7.3
7	7	-4	5.2	-5.2
7	6	-1	3.6	4.9
7	6	-2	2.6	3.4
7	6	-3	3.C	3.0
7	6	-4	4.6	4.6
7	5	-1	11.8	10.9
7	5	-2	7.9	7.7
7	5	-3	9.4	9.3
7	5	-4	10.7	10.4
7	4	0	3.8	4.0
7	4	-1	11.2	10.2
7	4	-2	12.1	12.3
7	4	-3	6.6	-7.3
7	4	-4	10.7	10.6
7	3	-1	11.6	11.6
7	3	-2	3.7	3.2
7	3	-3	5.8	6.4
7	3	-4	5.6	5.9
7	2	-1	5.6	6.8
7	2	-2	12.9	12.8
7	2	-3	3.6	3.8
7	2	-4	13.2	13.1
7	1	-1	9.6	9.2
7	1	-2	3.C	-3.4
7	1	-3	7.7	-2.7
7	1	-4	7.0	7.0
7	0	-5	12.5	12.5
7	0	-4	4.2	4.1
7	0	-3	12.7	12.5
7	0	-2	11.7	11.8
6	8	-1	3.C	3.4
6	8	-2	3.C	3.4
6	7	-1	15.8	15.8
6	7	-2	5.1	6.1
6	7	-3	7.7	7.3
6	7	-4	5.2	-5.2
6	6	-1	3.6	4.9
6	6	-2	2.6	3.4
6	6	-3	3.C	3.0
6	6	-4	4.6	4.6
6	5	-1	11.8	10.9
6	5	-2	7.9	7.7
6	5	-3	9.4	9.3
6	5	-4	10.7	10.4
6	4	0	3.8	4.0
6	4	-1	11.2	10.2
6	4	-2	12.1	12.3
6	4	-3	6.6	-7.3
6	4	-4	10.7	10.6
6	3	-1	11.6	11.6
6	3	-2	3.7	3.2
6	3	-3	5.8	6.4
6	3	-4	5.6	5.9
6	2	-1	5.6	6.8
6	2	-2	12.9	12.8
6	2	-3	3.6	3.8
6	2	-4	13.2	13.1
6	1	-1	9.6	9.2
6	1	-2	3.C	-3.4
6	1	-3	7.7	-2.7
6	1	-4	7.0	7.0
6	0	-5	12.5	12.5
6	0	-4	4.2	4.1
6	0	-3	12.7	12.5
6	0	-2	11.7	11.8
5	8	-1	3.C	3.4
5	8	-2	3.C	3.4
5	7	-1	15.8	15.8
5	7	-2	5.1	6.1
5	7	-3	7.7	7.3
5	7	-4	5.2	-5.2
5	6	-1	3.6	4.9
5	6	-2	2.6	3.4
5	6	-3	3.C	3.0
5	6	-4	4.6	4.6
5	5	-1	11.8	10.9
5	5	-2	7.9	7.7
5	5	-3	9.4	9.3
5	5	-4	10.7	10.4
5	4	0	3.8	4.0
5	4	-1	11.2	10.2
5	4	-2	12.1	12.3
5	4	-3	6.6	-7.3
5	4	-4	10.7	10.6
5	3	-1	11.6	11.6
5	3	-2	3.7	3.2
5	3	-3	5.8	6.4
5	3	-4	5.6	5.9
5	2	-1	5.6	6.8
5	2	-2	12.9	12.8
5	2	-3	3.6	3.8
5	2	-4	13.2	13.1
5	1	-1	9.6	9.2
5	1	-2	3.C	-3.4
5	1	-3	7.7	-2.7
5	1	-4	7.0	7.0
5	0	-5	12.5	12.5
5	0	-4	4.2	4.1
5	0	-3	12.7	12.5
5	0	-2	11.7	11.8
4	8	-1	3.C	3.4
4	8	-2	3.C	3.4
4	7	-1	15.8	15.8
4	7	-2	5.1	6.1
4	7	-3	7.7	7.3
4	7	-4	5.2	-5.2
4	6	-1	3.6	4.9
4	6	-2	2.6	3.4
4	6	-3	3.C	3.0
4	6	-4	4.6	4.6
4	5	-1	11.8	10.9
4	5	-2	7.9	7.7
4	5	-3	9.4	9.3
4	5	-4	10.7	10.4
4	4	0	3.8	4.0
4	4	-1	11.2	10.2
4	4	-2	12.1	12.3
4	4	-3	6.6	-7.3
4	4	-4	10.7	10.6
4	3	-1	11.6	11.6
4	3	-2	3.7	3.2
4	3	-3	5.8	6.4
4	3	-4	5.6	5.9
4	2	-1	5.6	6.8
4	2	-2	12.9	12.8
4	2	-3	3.6	3.8
4	2	-4	13.2	13.1
4	1	-1	9.6	9.2
4	1	-2	3.C	-3.4
4	1	-3	7.7	-2.7
4	1	-4	7.0	7.0
4	0	-5	12.5	12.5
4	0	-4	4.2	4.1
4	0	-3	12.7	12.5
4	0	-2	11.7	11.8
3	8	-1	3.C	3.4
3	8	-2	3.C	3.4
3	7	-1	15.8	15.8
3	7	-2	5.1	6.1
3	7	-3	7.7	7.3
3	7	-4	5.2	-5.2
3	6	-1	3.6	4.9
3	6	-2	2.6	3.4
3	6	-3	3.C	3.0
3	6	-4	4.6	4.6
3	5	-1	11.8	10.9
3	5	-2	7.9	7.7
3	5	-3	9.4	9.3
3	5	-4	10.7	10.4
3	4	0	3.8	4.0
3	4	-1	11.2	10.2
3	4	-2	12.1	12.3
3	4	-3	6.6	-7.3
3	4	-4	10.7	10.6
3	3	-1	11.6	11.6
3	3	-2	3.7	3.2
3	3	-3	5.8	6.4
3	3	-4	5.6	5.9
3	2	-1	5.6	6.8
3	2	-2	12.9	12.8
3	2	-3	3.6	3.8
3	2	-4	13.2	13.1
3	1	-1	9.6	9.2
3	1	-2	3.C	-3.4
3	1	-3	7.7	-2.7
3	1	-4	7.0	7.0
3	0	-5	12.5	12.5
3	0	-4	4.2	4.1
3	0	-3	12.7	12.5
3	0	-2	11.7	11.8
2	8	-1	3.C	3.4
2	8	-2	3.C	3.4
2	7	-1	15.8	15.8
2	7	-2	5.1	6.1
2	7	-3	7.7	7.3
2	7	-4	5.2	-5.2
2	6	-1	3.6	4.9
2	6	-2	2.6	3.4
2	6	-3	3.C	3.0
2	6	-4	4.6	4.6
2	5	-1	11.8	10.9
2	5	-2	7.9	7.7
2	5	-3	9.4	9.3
2	5	-4	10.7	10.4
2	4	0	3.8	4.0
2	4	-1	11.2	10.2
2	4	-2	12.1	12.3
2	4	-3	6.6	-7.3
2	4	-4	10.7	10.6
2	3	-1	11.6	11.6
2	3	-2	3.7	3.2
2	3	-3	5.8	6.4
2	3	-4	5.6	5.9
2	2	-1	5.6	6.8
2	2	-2	12.9	12.8
2	2	-3	3.6	3.8
2	2	-4	13.2	13.1
2	1	-1	9.6	9.2
2	1	-2	3.C	-3.4
2	1	-3	7.7	-2.7
2	1	-4	7.0	7.0
2	0	-5	12.5	12.5
2	0	-4	4.2	4.1
2	0	-3	12.7	12.5
2	0	-2	11.7	11.8
1	8	-1	3.C	3.4
1	8	-2	3.C	3.4
1	7	-1	15.8	15.8
1	7	-2	5.1	6.1
1	7	-3	7.7	7.3
1	7	-4	5.2	-5.2
1	6	-1	3.6	4.9
1	6	-2	2.6	3.4
1	6	-3	3.C	3.0
1	6	-4	4.6	4.6
1	5	-1	11.8	10.9
1	5	-2	7.9	7.7
1	5	-3	9.4	9.3
1	5	-4	10.7	10.4
1	4	0	3.8	4.0
1	4	-1	11.2	10.2
1	4	-2	12.1	12.3
1	4	-3	6.6	-7.3
1	4	-4	10.7	10.6
1	3	-1	11.6	11.6
1	3	-2	3.7	3.2
1	3	-3	5.8	6.4
1	3	-4	5.6	5.9
1	2	-1	5.6	6.8
1	2	-2	12.9	12.8
1	2	-3	3.6	3.8
1	2	-4	13.2	13.1
1	1	-1	9.6	9.2
1	1	-2	3.C	-3.4
1	1	-3	7.7	-2.7
1	1	-4	7.0	7.0
1	0	-5	12.5	12.5
1	0	-4	4.2	4.1
1	0	-3	12.7	12.5
1	0	-2	11.7	11.8
0	8	-1	3.C	3.4
0	8	-2	3.C	3.4
0	7	-1	15.8	15.8
0	7	-2	5.1	6.1
0	7	-3	7.7	7.3
0	7	-4	5.2	-5.2
0	6	-1	3.6	4.9
0	6	-2	2.6	3.4
0	6	-3	3.C	3.0
0	6	-4	4.6	4.6
0	5	-1	11.8	10.9
0	5	-2	7.9	7.7
0	5	-3	9.4	9.3
0	5	-4	10.7	10.4
0	4	0	3.8	4.0
0	4	-1	11.2	10.2
0	4	-2	12.1	12.3
0	4	-3	6.6	-7.3
0	4	-4	10.7	10.6
0	3	-1	11.6	11.6
0	3	-2	3.7	3.2
0	3	-3	5.8	6.4
0	3	-4	5.6	5.9
0	2	-1	5.6	6.8
0	2	-2	12.9	12.8
0	2	-3	3.6	3.8
0	2	-4	13.2	13.1
0	1	-1	9.6	9.2
0	1	-2	3.C	-3.4
0	1	-3	7.7	-2.7
0	1	-4	7.0	7.0
0	0	-5	12.5	12.5
0	0	-4	4.2	4.1
0	0	-3	12.7	12.5
0	0	-2	11.7	11.8

H	K	L	F OBS	F CALC
4	8	3	13.5	-14.0
4	8	2	17.1	17.3
4	8	1	10.1	-11.5
4	8	0	4.5	3.3
4	8	-1	27.3	27.0
4	8	-2	24.5	23.7
4	8	-3	11.0	11.2
4	8	-4	26.6	26.1
4	8	-5	4.9	4.4
4	8	-6	22.8	23.6
4	8	-7	10.2	9.9
4	8	-8	3.7	-1.6
4	7	7	10.2	10.5
4	7	6	15.3	16.0
4	7	5	10.4	9.7
4	7	4	29.5	30.0
4	7	3	4.0	3.3
4	7	2	14.1	13.7
4	7	1	19.4	18.4
4	7	0	34.3	35.5
4	7	-1	24.3	-20.7
4	7	-2	42.2	42.0
4	7	-3	10.1	10.9
4	7	-4	9.4	-9.5
4	7	-5	31.8	32.2
4	7	-7	18.6	18.4
4	7	-8	7.2	6.9
4	6	6	8.4	8.5
4	6	5	2.4	2.7
4	6	3	12.0	12.8
4	6	2	12.3	-16.0
4	6	1	10.7	10.9
4	6	0	21.8	20.4
4	6	-1	3.0	2.2
4	6	-2	27.5	26.9
4	6	-3	16.2	-16.0
4	6	-4	16.2	16.3
4	6	-5	5.2	5.4
4	6	-6	9.6	9.9
4	6	-8	15.3	15.7
4	5	5	12.3	12.5
4	5	4	12.0	12.8
4	5	3	10.7	10.9
4	5	2	12.0	12.8
4	5	1	19.4	20.0
4	5	0	4.2	4.4
4	5	-1	3.0	2.2
4	5	-2	12.3	12.5
4	5	-3	45.7	44.2
4	5	-4	2.1	-3.9
4	5	-5	16.6	16.8
4	5	-6	2.6	-2.0
4	5	-7	19.8	19.8
4	5	-8	7.5	7.5
4	5-10		3.8	0.8
4	4	8	11.1	10.4
4	4	6	17.7	18.0
4	4	5	3.7	4.0
4	4	4	11.5	11.8
4	4	3	4.7	4.8
4	4	2	13.7	14.8
4	4	1	8.3	8.3
4	4	0	31.6	32.3
4	4	-1	7.0	6.1
4	4	-2	47.2	48.6
4	4	-3	7.1	6.9
4	4	-4	37.8	36.4
4	4	-5	3.3	-2.7
4	4	-6	19.2	19.0
4	4	-7	9.1	10.1
4	4	-8	27.1	26.7
4	4	-9	3.3	2.6
4	4	-10	10.3	9.3
4	3	7	7.1	8.3
4	3	6	14.2	14.0
4	3	5	14.9	15.3
4	3	3	17.2	17.7
4	3	1	21.9	22.9
4	3	0	26.6	-25.0
4	3	-1	24.8	23.3
4	3	-2	17.2	16.9
4	3	-3	36.4	34.7
4	3	-4	4.6	-3.7
4	3	-5	2.4	3.8
4	3	-6	6.3	-5.3
4	3	-7	9.2	9.5
4	3	-9	31.5	31.3
4	3	-10	4.3	3.1
4	2	8	7.5	7.9
4	2	6	10.6	11.2
4	2	5	25.2	25.1
4	2	3	3.0	2.5
4	2	2	24.6	25.1
4	2	1	6.5	-6.4
4	2	0	19.2	18.6
4	2	-1	39.7	-39.7
4	2	-2	44.6	42.1
4	2	-3	2.5	1.0
4	2	-4	41.2	40.6
4	2	-5	11.0	-10.9
4	2	-6	24.6	24.9
4	2	-7	3.0	3.3
4	2	-8	12.4	12.5
4	2	-9	5.5	5.4
4	2	-10	14.1	13.6
4	1	7	8.1	7.1
4	1	6	16.2	16.2
4	1	5	19.4	20.4
4	1	4	3.6	-2.7
4	1	3	51.4	53.3
4	1	2	2.2	0.9
4	1	1	53.4	53.7
4	1	0	17.8	-17.3
4	1	-1	74.5	76.4
4	1	-2	12.3	11.8
4	1	-3	30.3	29.2
4	1	-4	4.1	3.0
4	1	-5	24.2	24.6
4	1	-6	8.8	-8.2
4	1	-7	5.5	5.4
4	1	-8	9.5	-9.6
4	0	8	12.4	12.5
4	0	7	2.5	3.5
4	0	6	13.8	14.3
4	0	4	19.8	40.7
4	0	2	13.6	14.7
4	0	0	13.2	-11.2
4	0	-2	7.8	7.5
4	0	-4	28.2	27.6
4	0	-6	10.8	10.6
4	0	-10	9.1	8.5
3	17	+2	3.4	-0.0
3	16	+1	4.4	0.2
3	15	7	4.4	4.1
3	15	1	9.1	9.7
3	15	-1	4.3	5.5
3	15	-2	4.6	-3.2
3	15	-3	11.0	11.6
3	15	-4	10.2	10.9
3	14	3	3.2	-3.3
3	14	2	14.5	14.2
3	14	1	3.6	2.1
3	14	0	5.4	5.8
3	14	-1	3.5	2.5
3	14	-2	9.4	10.2
3	14	-3	12.4	12.1
3	14	-4	5.5	6.2
3	13	3	10.1	10.7
3	13	2	5.9	5.9
3	13	1	17.2	17.3
3	13	-1	16.8	16.5
3	13	-2	2.8	-1.6
3	13	-3	22.1	22.0
3	13	-4	5.5	-4.5
3	12	+5	6.7	6.9
3	12	+4	8.5	-8.0
3	12	4	8.5	8.4
3	12	2	10.6	11.2
3	12	1	7.2	7.4
3	12	0	8.3	8.1
3	12	-1	4.8	-3.4
3	12	-2	10.4	10.8
3	12	-4	11.9	11.4
3	12	-5	2.5	2.4
3	12	-6	8.8	9.1
3	12	-7	4.9	5.4
3	12	-8	5.3	5.0
3	11	5	9.2	9.5
3	11	4	4.4	4.7
3	11	3	17.1	17.8
3	11	2	9.3	9.9
3	11	1	5.4	5.1
3	11	0	6.2	6.5
3	11	-1	22.9	21.9
3	11	-2	6.2	6.5
3	11	-3	20.4	20.5
3	11	-4	9.8	-8.4
3	11	-5	3.7	5.4
3	11	-6	7.7	8.0
3	11	-7	2.1	-2.4
3	10	6	11.1	11.7
3	10	5	3.0	-0.0
3	10	4	27.0	28.1
3	10	3	3.4	-3.4
3	10	2	20.4	20.5
3	10	1	7.8	8.3
3	10	0	9.3	9.0
3	10	-1	8.6	-8.9
3	10	-2	10.0	10.3
3	10	-3	11.0	11.3
3	10	-4	14.8	15.5
3	9	7	3.4	3.4
3	9	6	28.4	29.0
3	9	5	12.5	12.3
3	9	4	12.5	12.8
3	9	3	28.2	28.9
3	9	1	12.5	12.3
3	9	0	7.7	7.3
3	9	-1	14.3	13.7
3	9	-2	14.4	-13.9
3	9	-3	10.5	9.7
3	9	-4	9.3	-8.6
3	8	8	22.8	23.0
3	8	7	11.1	-11.0
3	8	6	9.0	8.9
3	8	5	17.7	17.3
3	8	4	13.7	14.9
3	8	3	2.1	-1.1
3	8	2	18.1	18.6
3	8	1	19.5	19.7
3	8	0	3.8	3.3
3	8	-1	22.3	22.5
3	8	-2	25.0	24.7
3	8	-3	5.4	-5.4
3	8	-4	13.7	14.9
3	8	-5	3.7	-4.0
3	8	-6	10.8	10.8
3	8	-7	3.7	3.7
3	7	7	5.5	-4.7
3	7	5	15.2	16.5
3	7	3	25.1	25.6
3	7	2	1.9	2.6
3	7	1	44.1	44.0
3	7	0	21.1	20.8
3	7	-1	48.4	47.5
3	7	-2	26.5	-26.2
3	7	-3	32.2	32.0
3	7	-4	9.5	-8.8
3	7	-5	37.0	37.6
3	7	-6	9.1	9.3
3	7	-7	16.0	17.2
3	6	6	7.9	8.0
3	6	5	3.2	-2.0
3	6	4	12.9	13.0
3	6	3	14.5	-19.2
3	6	2	5.8	6.0
3	6	1	5.8	5.9
3	6	0	26.0	26.4
3	6	-1	2.4	-1.0
3	6	-2	23.2	22.4
3	6	-3	14.1	-13.8
3	6	-4	19.3	19.5
3	6	-5	2.0	3.8
3	6	-6	8.8	9.1
3	6	-7	4.9	5.4
3	6	-8	9.9	10.2
3	5	7	8.4	8.2
3	5	6	25.3	26.0
3	5	5	2.6	-1.5
3	5	4	14.5	14.8
3	5	3	3.0	-0.0
3	5	2	27.4	27.2
3	5	1	5.4	5.3
3	5	0	5.9	6.0
3	5	-1	5.4	-5.8
3	5	-2	7.4	7.6
3	5	-3	13.4	13.6
3	5	-4	16.4	16.5
3	5	-5	2.4	-2.0
3	5	-6	7.0	7.5
3	5	-7	17.9	17.9
3	4	8	9.7	9.7
3	4	7	7.4	7.4
3	4	6	11.1	11.1
3	4	5	12.7	12.9
3	4	4	3.7	3.5
3	4	3	6.6	-5.4
3	4	2	11.4	-10.9
3	4	1	11.6	11.9
3	4	0	4.7	4.5
3	4	-1	14.6	14.8
3	4	-2	15.7	15.9
3	4	-3	4.7	-4.2
3	4	-4	11.6	11.8
3	4	-5	4.7	4.6
3	4	-6	4.7	4.6
3	4	-7	4.7	4.6
3	3	7	4.7	4.6
3	3	6	4.7	4.6
3	3	5	4.7	4.6
3	3	4	4.7	4.6
3	3	3	4.7	4.6
3	3	2	4.7	4.6
3	3	1	4.7	4.6
3	3	0	4.7	4.6
3	3	-1	4.7	4.6
3	3	-2	4.7	4.6
3	3	-3	4.7	4.6
3	3	-4	4.7	4.6
3	3	-5	4.7	4.6
3	3	-6	4.7	4.6
3	3	-7	4.7	4.6
3	2	8	4.7	4.6
3	2	7	4.7	4.6
3	2	6	4.7	4.6
3	2	5	4.7	4.6
3	2	4	4.7	4.6
3	2	3	4.7	4.6
3	2	2	4.7	4.6
3	2	1	4.7	4.6
3	2	0	4.7	4.6
3	2	-1	4.7	4.6
3	2	-2	4.7	4.6
3	2	-3	4.7	4.6
3	2	-4	4.7	4.6
3	2	-5	4.7	4.6
3	2	-6	4.7	4.6
3	2	-7	4.7	4.6
3	2	-8	4.7	4.6
3	1	7	4.7	4.6
3	1	6	4.7	4.6
3	1	5	4.7	4.6
3	1	4	4.7	4.6
3	1	3	4.7	4.6
3	1	2	4.7	4.6
3	1	1	4.7	4.6
3	1	0	4.7	4.6
3	1	-1	4.7	4.6
3	1	-2	4.7	4.6
3	1	-3	4.7	4.6
3	1	-4	4.7	4.6
3	1	-5	4.7	4.6
3	1	-6	4.7	4.6
3	1	-7	4.7	4.6
3	1	-8	4.7	4.6
3	0	8	4.7	4.6
3	0	7	4.7	4.6
3	0	6	4.7	4.6
3	0	5	4.7	4.6
3	0	4	4.7	4.6
3	0	3	4.7	4.6
3	0	2	4.7	4.6
3	0	1	4.7	4.6
3	0	0	4.7	4.6
3	0	-1	4.7	4.6
3	0	-2	4.7	4.6
3	0	-3	4.7	4.6
3	0	-4	4.7	4.6
3	0	-5	4.7	4.6
3	0	-6	4.7	4.6
3	0	-7	4.7	4.6
3	0	-8	4.7	4.6
2	8	5	2.7	-2.6
2	8	4	10.2	11.1
2	8	3	17.3	-18.4
2	8	2	28.8	30.0
2	8	1	7.8	8.1
2	8	0	24.8	23.9
2	8	-1	8.7	-7.6
2	8	-2	51.0	50.2
2	8	-4	20.7	22.0
2	8	-5	2.0	-1.6
2	8	-6	8.4	7.9
2	8	-8	9.5	9.4
2	7	7	7.2	7.2
2	7	6	2.5	4.2
2	7	5	2.7	0.4
2	7	4	9.6	9.7
2	7	3	5.3	4.4
2	7	2	14.2	15.4
2	7	1	10.1	9.8
2	7	0	2.0	0.8
2	7	-1	21.9	22.2
2	7	-2	4.0	3.8
2	7	-3	3.4	-3.4
2	7	-4	27.0	28.1
2	7	-5	13.8	14.1
2	7	-6	2.0	0.8
2	7	-7	21.9	22.2
2	6	6	4.0	3.8
2	6	5	10.8	11.8
2	6	4	17.9	-17.2
2	6	3	6.0	6.9
2	6	2	30.3	32.3
2	6	1	9.2	-9.3
2	6	0	26.9	-26.5
2	6	-1	55.5	54.9
2	6	-2	27.6	-26.4
2	6	-3	23.3	22.3
2	6	-4	13.1	-11.7
2	6	-5	46.2	45.0
2	6	-6	4.1	-4.4
2	6	-8	16.2	16.3
2	5	5	17.9	-17.2
2	5	4	6.0	6.9
2	5	3	26.9	-26.5
2	5	2	9.2	-9.3
2	5	1	23.1	24.2
2	5	0	10.6	-12.1
2	5	-1	34.9	34.9
2	5	-2	17.5	-18.6
2	5	-3	10.8	10.4
2	5	-4	7.7	-7.9
2	5	-5	9.5	9.1
2	5	-6	9.8	9.1
2	4	7	5.9	4.5
2	4	6	4.1	-4.7
2	4	5	8.9	8.6
2	4	4	10.8	11.8
2	4	3	26.9	28.1
2	4	2	13.8	12.4
2	4	1	23.8	22.8
2	4	0	38.3	-38.2
2	4	-1	45.6	43.5
2	4	-2	27.9	25.9
2	4	-3	79.5	78.5
2	4	-4	9.3	9.5
2	4	-5	120.2	121.2
2	4	-7	18.4	18.3
2	4	-8	12.7	-12.3
2	4	-9	11.3	11.3
2	4	-10	3.8	-2.7
2	3	8	16.0	14.2
2	3	7	2.2	2.2
2	3	6	19.2	19.8
2	3	5	11.8	-12.7
2	3	4	39.2	41.2
2	3	3	17.1	18.4
2	3	2	59.3	60.5
2	3	1	19.6	18.5
2	3	0	42.4	41.9
2	3	-1	20.7	19.7
2	3	-2	26.5	21.4
2	3	-3	42.2	45.9
2	3	-4	39.4	38.8
2	3	-5	20.0	20.6
2	3	-6	19.4	19.1
2	3	-7	2.5	+0.5
2	3	-8	12.1	11.1
2	3	-9	3.0	-0.8
2	3	-10	9.5	8.5
2	2	8	19.6	19.7
2	2	7	5.5	-5.4
2	2	6	19.2	17.3
2	2	5	3.8	-2.9
2	2	4	122.7	124.3
2	2	3	11.7	-10.9
2	2	2	19.4	19.7
2	2	1	3.2	2.9
2	2	0	32.9	32.4
2	2	-1	63.9	-64.9
2	2	-2	57.1	56.2
2	2	-3	13.2	-12.5
2	2	-4	34.4	34.3
2	2	-5	22.4	23.4
2	2	-6	69.2	69.0
2	2	-7	7.2	7.2
2	2	-8	16.2	15.4
2	2	-9	12.4	-11.7
2	2	-10	3.8	4.2
2	1	8	19.6	19.7
2	1	7	9.5	-9.4
2	1	6	19.9	17.3
2	1	5	3.8	-2.9
2	1	4	122.7	124.3
2	1	3	19.4	19.7
2	1	2	3.2	2.9
2	1	1	32.9	32.4
2	1	0	63.9	-64.9
2	1	-1	57.1	56.2
2	1	-2	13.2	-12.5
2	1	-3	34.4	34.3
2	1	-4	22.4	23.4
2	1	-5	69.2	69.0
2	1	-6	7.2	7.2
2	1	-7	16.2	15.4
2	1	-8	12.4	-11.7
2	1	-9	3.0	-0.8
2	1	-10	9.5	8.5
2	0	8	19.6	19.7
2	0	7	9.5	-9.4
2	0	6	19.9	17.3
2	0	5	3.8	-2.9
2	0	4	122.7	124.3
2	0	3	19.4	19.7
2	0	2	3.2	2.9
2	0	1	32.9	32.4
2	0	0	63.9	-64.9
2	0	-1	57.1	56.2
2	0	-2	13.2	-12.5
2	0	-3	34.4	34.3
2	0	-4	22.4	23.4
2	0	-5	69.2	69.0
2	0	-6	7.2	7.2
2	0	-7	16.2	15.4
2	0	-8	12.4	-11.7
2	0	-9	3.0	-0.8
2	0	-10	9.5	8.5
1	16	2	5.5	9.2
1	16	0	10.9	10.4
1	16	-1	4.2	3.9
1	16	-2	3.0	3.1
1	15	3	13.7	13.7
1	15	1	14.2	14.5
1	15	-1	3.9	4.6
1	15	-2	11.3	11.2
1	15	-3	3.3	3.4
1	14	4	14.2	13.7
1	14	3	4.1	4.4
1	14	2	19.1	19.0
1	14	1	2.6	2.6
1	14	0	11.7	11.4
1	14	-1	14.2	13.9
1	14	-2	15.1	14.9
1	14	-3	3.3	-2.6
1	14	-4	9.4	9.2
1	13	5	9.4	9.2
1	13	4	4.5	-4.5
1	13	3	11.0	11.2
1	13	2	4.3	4.1
1	13	1	10.4	9.6
1	13	-1	5.6	5.9
1	13	-2	17.0	17.1
1	13	-4	7.9	7.6
1	12	6	2.1	-0.5
1	12	5	12.7	12.5
1	12	4	3.9	-2.4
1	12	3	10.9	10.9
1	12	2	20.4	21.1
1	12	1	6.8	-6.8
1	12	0	19.1	18.3
1	12	-1	4.6	3.8
1	12	-2	23.3	23.6
1	12	-3	8.0	-7.7
1	12	-4	16.4	16.8
1	12	-6	12.7	12.9
1	11	7	10.4	10.5
1	11	6	7.2	6.4
1	11	5	7.2	6.4
1	11	4	9.7	9.9
1	11	2	8.9	9.6
1	11	1	8.7	8.2
1	11	0	8.7	8.5
1	11	-1	20.8	19.6
1	11	-2	13.8	14.7
1	11	-3	28.9	29.7
1	11	-4	2.6	1.0
1	11	-5	21.3	20.9
1	11	-6	9.4	8.2
1	11	-7	7.5	9.1
1	10	4	12.7	14.1
1	10	3	6.3	8.6
1	10	2	22.9	23.3
1	10	1	11.7	-12.6
1	10	0	31.7	30.2
1	10	-1	24.1	-23.2
1	10	-2	16.4	17.0
1	10	-3	13.6	-14.6
1	10	-4	15.7	16.6
1	10	-5	9.5	9.7
1	10	-6	9.8	9.4
1	10	-7	4.2	5.2
1	10	-8	7.5	7.9
1	9	7	7.2	8.3
1	9	6	3.0	-0.1
1	9	5	7.5	7.3
1	9	4	17.5	-18.6
1	9	3	10.8	10.4
1	9	2	9.2	-9.3
1	9	1	33.7	34.6
1	9	0	2.2	2.7
1	9	-1	37.9	37.2
1	9	-2	2.8	2.7
1	9	-3	18.6	18.9
1	9	-4	7.0	7.6
1	9	-5	28.2	29.2
1	9	-7	17.0	16.9
1	8	-4	3.4	1.1
1	8	8	14.3	14.3
1	8	7	9.3	8.8
1	8	6	16.5	17.3
1	8	5	10.8	11.8
1	8	4	25.9	26.7
1	8	3	6.4	7.4
1	8	2	20.2	20.5
1	8	1	6.0	6.6
1	8	0	48.4	49.6
1	8	-1	23.7	-22.7
1	8	-2	8.8	9.2
1	8	-4	17.9	17.8
1	8	-6	14.9	14.9
1	8	-7	17.7	17.8
1	8	-8	7.8	7.6
1	7	8	3.2	-3.2
1	7	7	10.9	11.7
1	7	6	5.1	5.3
1	7	5	18.9	20.1
1	7	4	10.3	-12.0
1	7	3	18.2	19.3
1	7	2	20.9	-22.1
1	7	1	29.4	29.1
1	7	0	14.3	13.7
1	7	-1	24.5	23.9
1	7	-2	2.5	3.4
1	7	-3	6.7	-6.5
1	7	-4	15.4	15.5
1	7	-6	9.9	-8.9
1	7	-7	15.2	14.7
1	6	8	6.9	6.1
1	6	7	2.5	1.7
1	6	6	28.5	27.5
1	6	5	14.0	14.6
1	6	4	37.8	40.0
1	6	3	19.4	-18.9
1	6	2	49.3	49.1
1	6	1	1.9	-0.1
1	6	0	45.0	-42.9
1	6	-1	14.2	12.6
1	6	-2	41.9	41.7
1	6	-3	27.7	29.1
1	6	-4	19.1	-15.7
1	6	-5	18.4	20.9
1	6	-7	4.5	4.2
1	5	-8	12.4	12

TABLE 11

$Ni(py)_2(NO_3)_2(H_2O)_2$

Atom positions (fractional coordinates)

	x/a	y/b	z/c
Ni	0.00000(-)	0.00000(-)	0.00000(-)
C(1)	0.3525(5)	0.0331(3)	0.1484(6)
C(2)	0.4998(5)	-0.0853(4)	0.2003(6)
C(3)	0.5082(5)	-0.2019(4)	0.1701(7)
C(4)	0.3693(5)	-0.2597(3)	0.0908(7)
C(5)	0.2264(4)	-0.2012(3)	0.0449(6)
O(1)	0.0731(3)	0.1101(2)	0.2289(3)
O(2)	0.1464(4)	-0.0183(2)	0.4465(4)
O(3)	0.1438(3)	0.1607(2)	0.5159(3)
O(4)	0.1069(3)	0.1200(2)	-0.1239(4)
N(1)	0.1209(3)	0.0819(2)	0.3982(4)
N(2)	0.2162(3)	-0.0891(2)	0.0726(4)

TABLE 12

$Ni(py)_2(NO_3)_2(H_2O)_2$

(a) Anisotropic temperature factors *

	U_{11}	U_{22}	U_{33}	$2U_{32}$	$2U_{31}$	$2U_{12}$
Ni	0.027	0.017	0.022	0.000	0.000	0.000
C(1)	0.036	0.030	0.046	-0.005	0.023	-0.006
C(2)	0.036	0.039	0.059	-0.008	0.017	-0.007
C(3)	0.035	0.040	0.066	0.004	0.023	0.013
C(4)	0.040	0.028	0.078	-0.008	0.021	0.009
C(5)	0.031	0.031	0.048	-0.009	0.015	-0.004
O(1)	0.051	0.026	0.022	-0.001	0.013	0.005
O(2)	0.058	0.024	0.041	0.012	0.026	0.017
O(3)	0.054	0.025	0.026	-0.012	0.015	-0.004
O(4)	0.045	0.024	0.028	-0.001	0.028	-0.012
N(1)	0.030	0.023	0.026	0.001	0.016	0.001
N(2)	0.032	0.024	0.031	-0.004	0.018	-0.004

(b) Mean estimated standard deviations ($Å^2$)

Ni	0.0002	0.0002	0.0002	-	-	-
C	0.002	0.002	0.002	0.003	0.003	0.003
O	0.002	0.001	0.001	0.002	0.002	0.002
N	0.001	0.001	0.001	0.002	0.002	0.002

* These are the values of U_{ij} in equation (5) (Section I.1.4(b)).

TABLE 13

$Ni(py)_2(NO_3)_2(H_2O)_2$

Hydrogen positions * (fractional coordinates) and isotropic temperature factors ($Å^2$)

H(1)	C(1)	0.3424(54)	0.0507(41)	0.1670(63)	0.014(12)
H(2)	C(2)	0.5991(55)	-0.0363(41)	0.2581(64)	0.019(11)
H(3)	C(3)	0.6139(69)	-0.2401(51)	0.2084(78)	0.038(15)
H(4)	C(4)	0.3629(61)	-0.3348(47)	0.0552(73)	0.037(10)
H(5)	C(5)	0.1293(48)	-0.2348(34)	-0.0101(54)	0.016(9)
H(6)	O(4)	0.0834(50)	0.1234(38)	-0.2419(65)	0.017(10)
H(7)	O(4)	0.1092(65)	0.1841(51)	-0.0990(77)	0.040(15)

* Hydrogens are bonded to atoms shown in square brackets

APPENDIX IV

EXPERIMENTAL

DINITRATOTRIS(PYRIDINE)-COBALT(II), -COPPER(II), -ZINC(II)

Preparation of Crystals

All three complexes were prepared by methods which have previously been described [141, 145, 170, 176, 179]. Crystals were obtained in each case from 1:1 ethanol-2,2-dimethoxypropane solutions containing a small amount of pyridine. To avoid atmospheric decomposition, the crystals were enclosed in thin-walled glass tubes.

Crystal Data

(I) $C_{15}H_{15}N_5O_6Co$

$M = 420.3$

Monoclinic

$a = 12.584 \pm 0.005$, $b = 9.435 \pm 0.004$, $c = 16.327 \pm 0.006$ Å, $\beta = 109.48 \pm 0.05^{\circ}$, $U = 1828$ Å^3

$D_m = 1.51$, $Z = 4$, $D_c = 1.53$

$F(000) = 860$

Space group $C2/c$ (C_{2h}^6, No 15) from systematic absences: $hk\ell$ for $h + k$ odd, $h0\ell$ for ℓ odd

Mo-K_α X-rays, $\lambda = 0.7107$ Å

μ(Mo-K_α) = 10.24 cm^{-1}

(II) $C_{15}H_{15}N_5O_6Zn$

M = 426.7

Monoclinic

a = 12.60 ± 0.03, b = 9.40 ± 0.03, c = 16.27 ± 0.03 Å,

β = 108.9 ± 0.2°, U = 1823 Å^3

D_m = 1.55, Z = 4, D_c = 1.55

F(000) = 872

Space group C2/c (C_{2h}^6, No 15) from systematic absences

Cu-K_α X-rays, λ = 1.5418 Å

μ(Cu-K_α) = 23.2 cm^{-1}

(III) $C_{15}H_{15}N_5O_6Cu$

M = 424.9

Monoclinic

a = 12.783 ± 0.006, b = 9.199 ± 0.005, c = 16.055

± 0.008 Å, β = 108.35 ± 0.03°, U = 1792 Å^3

D_m = 1.63, Z = 4, D_c = 1.66

F(000) = 868

Space group C2/c (C_{2h}^6, No 15) from systematic absences

Mo-K_α X-rays, λ = 0.7107 Å

μ (Mo-K_α) = 13.8 cm^{-1}

Crystallographic Measurements

The unit-cell parameters for all three complexes were initially determined from oscillation and Weissenberg photographs taken with Cu-K_α radiation, and from precession photographs taken with Mo-K_α radiation.

$Co(py)_3(NO_3)_2$ (I) and $Cu(py)_3(NO_3)_2$ (II). The preliminary unit-cell dimensions were adjusted by least-squares analysis of θ, χ, and ϕ setting angles of twelve reflections recorded on a Hilger and Watts Y290 four-circle diffractometer.

For the intensity measurements, zirconium-filtered molybdenum radiation was used and for the cobalt complex 2161 independent reflections were collected (1578 for the copper complex) by use of the θ-2θ scan technique. Of these some 1849 for the cobalt complex (1466 for Cu) were considered observed using the criteria $I \geqslant 1\sigma(I)$, where σ was determined from counter statistics. Values of I were corrected for Lorentz-polarisation effects but no corrections for absorption were made.

$Zn(py)_3(NO_3)_2$ (III). A small crystal was mounted about b and 1020 independent reflections from the reciprocal-lattice nets h0-8ℓ were recorded on equatorial and equi-inclination Weissenberg photographs by the multiple-film technique, and were estimated visually by comparison with a calibrated strip. After correction for Lorentz, polarisation, and rotation factors, the structure amplitudes were placed on an overall scale by comparison with values obtained from the hk0 reciprocal-lattice net recorded by precession methods. Unobserved reflections were not included in the calculations and absorption corrections were not applied.

Structure Determination and Refinement

(III) The structure of the zinc complex was solved by conventional Patterson and electron-density calculations with initial phasing based on the zinc atom and assuming the validity of space group C2/c (This assumption necessitates that the molecules possess two-fold symmetry). Several cycles of structure-factor and electron-density calculations effected preliminary refinement and reduced R to 0.19. An overall isotropic vibration parameter, U_{iso} (0.06 Å^2) was assigned to all the atoms.

The parameters obtained at the end of the refinement for the zinc complex were used for $Co(py)_3(NO_3)_2$ and $Cu(py)_3(NO_3)_2$ and several cycles of structure-factor and electron-density calculations reduced R to 0.25 (for Co) and 0.20 (for Cu).

For $Zn(py)_3(NO_3)_2$, the correctness of the space-group choice was examined by a trial refinement in space group Cc which converged when R was 0.10 but revealed disturbing discrepancies in bond lengths, in particular an aromatic C-C bond distance of 1.73 Å. In comparison, refinement in space group C2/c by full-matrix least-squares converged after 8 cycles with R 0.11 and R' 0.023. The resulting molecular geometry showed none of the anomalies produced by the previous refinement, thus justifying our choice of the latter space group.

(I) & (II) Statistical analyses of the data for (I) and (II) also favoured the centrosymmetric space group and refinement in C2/c by full-matrix least-squares converged after 8 cycles in each case with R 0.12 and R' 0.018 for Co, and R 0.11 and R' 0.021 for Cu. Removal of those planes for which $I \geqslant 2\sigma(I)$ left 1104 (Co) and 1138 (Cu) independent data, and structure-factor calculations using the final parameters resulted in R 0.07, R' 0.008 (Co), and R 0.08, R' 0.011 (Cu) (Details of the refinements are given in Table 14).

In all refinement cycles, the weighting scheme given as equation (32) (Section I.1.8(b)) was applied to the data. Initially, the p parameters were chosen to give unit weights to all reflections, but they were varied in later cycles as indicated by a $|F_o|$ and $(\sin\theta/\lambda)$ analysis of $\sum w\Delta^2$. The final values are: (I) p_1 100, p_2 0.01, p_3 0.0001, p_4 0; (II) p_1 50, p_2 0.001, p_3 0.0001, p_4 0; (III) p_1 50, p_2 0.1, p_3 0.0001, p_4 0.

In all the structure-factor calculations, the atomic scattering factors were taken from ref. 212. The observed and calculated structure factors are listed in Tables 15 (Co), 16 (Cu) and 17 (Zn). Fractional coordinates of all non-hydrogen atoms and the respective anisotropic temperature factors are given in Tables 18 (Co), 19 (Cu) and 20 (Zn).

The relevant interatomic dimensions and some calculated least-squares best planes through the molecules

are given in Section II.2.2. The estimated standard deviations recorded were derived from the inverse of the least-squares normal-equation matrix, and are probably best regarded as minimum values.

TABLE 14

Course of refinement

Complex	Cycles	Parameters refined	Final $\underline{R}$	Final $\underline{R}'$
	1 - 3	$\underline{x}$, $\underline{y}$, $\underline{z}$, $\underline{U}_{iso}$ for M, N, 0, C; layer scale factors for Zn, overall scale for Co and Cu, unit weights, full matrix		
Zn			0.141	0.034
Co			0.139	0.041
Cu			0.156	0.053
	4 - 5	$\underline{x}$, $\underline{y}$, $\underline{z}$, $\underline{U}_{iso}$ for M, N, 0, C; one overall scale, weighting scheme adjusted, full matrix		
Zn			0.135	0.028
Co			0.136	0.025
Cu			0.140	0.026
	6 - 8	$\underline{x}$, $\underline{y}$, $\underline{z}$, $\underline{U}_{ij}$ ($\underline{i}$, $\underline{j}$ = 1, 2, 3), for M, N, 0, C; small adjustments to weighting scheme, full matrix		
Zn			0.111	0.023
Co			0.123	0.018
Cu			0.114	0.021
	9	planes for which $I \geqslant 2\sigma(I)$ removed		
Co			0.072	0.008
Cu			0.081	0.011

TABLE 12

$Co(py)_3(NO_2)_2$

Observed and final-calculated structure amplitudes

H	K	L	F OBS	F CALC
11	2	-2	20.7	17.0
11	2	-3	6.1	-3.8
11	2	-4	11.0	-11.8
11	2	-5	11.0	11.4
11	2	-6	7.8	10.4
11	2	-7	12.1	-11.0
11	2	-8	9.3	12.2
11	2	-9	8.4	-6.5
11	2	-10	8.0	11.0
11	3	0	12.4	-6.2
11	3	-1	12.2	17.7
11	3	-2	20.6	-24.1
11	3	-3	18.0	-24.4
11	3	-4	4.4	11.5
11	3	-5	17.7	-16.7
11	3	-6	12.0	9.2
11	3	-7	12.5	9.2
11	3	-8	19.4	17.3
11	3	-9	11.9	-2.7
11	3	-10	14.4	8.4
11	3	-11	3.5	7.7
11	3	-12	9.6	-9.6
11	3	-13	14.2	-13.5
11	3	-14	13.7	14.0
11	3	-15	5.6	-12.1
11	3	-16	12.9	-7.8
11	4	1	13.5	8.4
11	4	2	5.5	1.7
11	4	3	6.5	-6.6
11	4	4	11.2	2.3
11	4	5	12.4	2.3
11	4	6	20.6	13.2
11	4	7	8.6	10.5
11	4	8	10.4	-11.5
11	4	9	12.9	-9.7
11	4	10	3.3	-9.7
11	4	11	10.4	-11.5
11	4	12	6.2	8.0
11	4	13	16.3	-6.2
11	4	14	22.9	-19.6
11	4	15	15.2	16.3
11	4	16	7.1	-2.6
11	5	1	15.9	14.2
11	5	2	13.4	-19.2
11	5	3	2.5	2.9
11	5	4	3.5	11.0
11	5	5	12.1	-11.9
11	5	6	16.8	-16.2
11	5	7	10.6	12.1
11	5	8	8.4	3.9
11	5	9	21.6	-16.1
11	5	10	10.2	8.1
11	5	11	14.6	22.1
11	5	12	15.6	10.2
11	5	13	12.6	-9.1
11	5	14	18.1	-17.9
11	5	15	13.9	-13.1
11	5	16	16.6	16.6
11	6	1	16.5	13.6
11	6	2	13.9	10.0
11	6	3	14.5	10.5
11	6	4	27.5	-21.0
11	6	5	13.1	-15.1
11	6	6	15.4	12.3
11	6	7	6.9	-4.2
11	6	8	13.3	-9.4
11	6	9	19.7	-17.7
11	6	10	23.9	23.4
11	6	11	10.1	17.2
11	6	12	27.6	-24.8
11	6	13	19.5	18.5
11	6	14	2.5	-7.1
11	6	15	14.1	-14.2
11	6	16	9.7	8.9
11	7	1	10.2	12.0
11	7	2	20.6	-20.2
11	7	3	20.3	23.5
11	7	4	36.1	-35.7
11	7	5	13.2	16.4
11	7	6	14.4	14.5
11	7	7	23.5	21.2
11	7	8	10.6	12.0
11	7	9	11.4	-11.1
11	7	10	12.2	11.9
11	7	11	9.1	-10.5
11	7	12	14.6	22.1
11	7	13	10.2	-2.9
11	7	14	11.5	-13.9
11	7	15	20.4	20.8
11	7	16	10.6	11.3
11	8	1	12.0	-10.5
11	8	2	14.5	-10.5
11	8	3	32.6	-27.1
11	8	4	12.3	12.8
11	8	5	32.4	32.5
11	8	6	5.5	-6.9
11	8	7	27.1	32.5
11	8	8	9.3	7.2
11	8	9	32.6	-27.1
11	8	10	12.3	-10.7
11	8	11	20.1	-25.6
11	8	12	32.7	41.1
11	8	13	17.9	-13.7
11	8	14	12.0	10.5
11	8	15	8.5	-11.1
11	8	16	15.5	-14.9
11	9	1	30.7	25.4
11	9	2	15.7	20.8
11	9	3	11.5	-13.9
11	9	4	10.6	-2.9
11	9	5	16.6	16.6
11	9	6	10.7	3.6
11	9	7	14.5	-14.5
11	9	8	10.7	-3.6
11	9	9	9.9	-13.1
11	9	10	15.8	14.5
11	9	11	19.7	-17.7
11	9	12	23.9	23.4
11	9	13	19.6	18.5
11	9	14	2.5	-7.1
11	9	15	14.1	-14.2
11	9	16	9.7	8.9
11	10	1	23.9	-23.4
11	10	2	26.8	-30.1
11	10	3	10.0	-10.5
11	10	4	19.5	19.0
11	10	5	19.4	-19.4
11	10	6	11.4	-4.1
11	10	7	17.2	17.8
11	10	8	4.0	9.3
11	10	9	11.7	4.0
11	10	10	17.2	17.8
11	10	11	36.1	-35.7
11	10	12	6.1	7.2
11	10	13	22.9	23.6
11	10	14	19.1	-12.9
11	10	15	7.8	-7.9
11	10	16	12.9	5.8
11	11	1	12.9	5.8
11	11	2	2.5	6.3
11	11	3	10.0	-13.1
11	11	4	5.0	-1.2
11	11	5	17.7	9.5
11	11	6	14.0	12.8
11	11	7	6.1	10.6
11	11	8	9.8	17.5
11	11	9	13.6	5.8
11	11	10	13.6	13.2
11	11	11	17.9	-13.7
11	11	12	10.5	10.5
11	11	13	8.5	-11.1
11	11	14	15.5	-14.9
11	11	15	27.8	27.6
11	11	16	18.1	-16.1
11	12	1	24.5	-25.8
11	12	2	4.10	9.9
11	12	3	35.8	33.8
11	12	4	14.2	6.7
11	12	5	28.6	-27.7
11	12	6	8.C	-7.5
11	12	7	20.7	23.7
11	12	8	7.7	7.7
11	12	9	22.5	18.1
11	12	10	3.2	2.2
11	12	11	27.5	-28.5
11	12	12	14.9	17.8
11	12	13	28.9	-30.2
11	12	14	10.4	-12.9
11	12	15	31.9	-33.5
11	12	16	10.4	34.6
11	13	1	19.6	-15.7
11	13	2	22.5	-20.1
11	13	3	16.5	16.0
11	13	4	21.6	16.2
11	13	5	14.0	-9.6
11	13	6	16.1	-8.6
11	13	7	12.8	8.2
11	13	8	17.5	19.7
11	13	9	20.4	-12.2
11	13	10	19.3	19.8
11	13	11	54.5	-61.2
11	13	12	60.8	63.4
11	13	13	30.4	-34.4
11	13	14	48.5	52.2
11	13	15	63.3	-64.4
11	13	16	52.2	50.3
11	14	1	39.4	42.2
11	14	2	42.9	-42.9
11	14	3	39.4	42.2
11	14	4	29.8	-29.2
10	0	-16	25.5	21.7
9	7	5	18.1	-7.7
9	7	4	13.8	-12.4
9	7	2	17.3	18.8
9	7	1	4.1	-4.6
9	7	-1	16.5	13.6
9	7	-3	28.0	-25.1
9	7	-4	14.3	-16.5
9	7	-5	12.4	16.3
9	7	-6	13.7	16.0
9	7	-7	15.3	1.7
9	7	-8	30.7	-29.7
9	7	-9	16.3	3.2
9	7	-10	6.4	13.0
9	7	-11	11.7	-13.7
9	7	-12	13.0	12.9
9	7	-13	15.9	-13.7
9	7	-14	6.2	-3.4
9	7	-15	15.9	-13.7
9	7	-16	6.2	-3.4
9	6	1	32.5	31.2
9	6	2	12.9	8.9
9	6	3	23.3	-22.7
9	6	4	43.1	42.4
9	6	5	2.1	5.8
9	6	6	23.3	-23.4
9	6	7	13.4	-13.3
9	6	8	14.4	-15.5
9	6	9	5.7	13.0
9	6	10	16.4	-16.0
9	6	11	14.4	-2.9
9	6	12	19.5	19.0
9	6	13	5.6	-12.1
9	6	14	15.9	17.3
9	6	15	18.4	-15.7
9	6	16	6.2	9.6
9	5	1	11.4	-4.1
9	5	2	34.6	31.6
9	5	3	7.4	4.1
9	5	4	9.3	9.3
9	5	5	21.7	27.2
9	5	6	15.4	14.4
9	5	7	23.3	21.2
9	5	8	8.9	1.1
9	5	9	17.0	17.8
9	5	10	16.4	-16.0
9	5	11	3.4	-11.7
9	5	12	17.0	16.0
9	5	13	6.3	-1.5
9	5	14	3.4	-11.7
9	5	15	17.0	16.0
9	5	16	6.3	-1.5
9	4	1	14.7	-10.7
9	4	2	25.1	-26.0
9	4	3	36.9	37.9
9	4	4	25.0	-26.0
9	4	5	39.8	-42.2
9	4	6	14.4	15.2
9	4	7	21.7	27.2
9	4	8	27.5	-28.5
9	4	9	21.2	-23.6
9	4	10	9.3	7.2
9	4	11	25.2	-23.6
9	4	12	12.2	9.1
9	4	13	16.7	10.1
9	4	14	39.5	44.0
9	4	15	18.5	19.7
9	4	16	9.4	-55.1
9	3	1	13.2	-1.9
9	3	0	8.4	-1.8
9	3	-1	18.1	13.1
9	3	-2	21.8	-23.6
9	3	-3	36.9	37.9
9	3	-4	27.5	-28.5
9	3	-5	21.2	-23.6
9	3	-6	41.2	40.8
9	3	-7	23.3	19.2
9	3	-8	45.6	-42.8
9	3	-9	9.5	4.6
9	3	-10	5.9	7.9
9	3	-11	32.6	34.5
9	3	-12	25.9	-27.4
9	3	-13	10.4	-9.7
9	3	-14	17.1	17.7
9	3	-16	11.6	-11.2
9	3	-17	13.2	-1.9
9	1	8	8.4	-1.8
9	1	6	3.8	13.1
9	1	5	21.8	-23.6
9	1	3	36.9	37.9
9	1	2	25.0	-26.0
9	1	1	39.8	-42.2
9	1	-2	12.2	9.1
9	1	-3	25.2	-23.6
9	1	-4	16.7	10.1
9	1	-5	39.5	44.0
9	1	-6	18.5	19.7
9	1	-7	9.4	-55.1
9	1	-8	10.8	14.5
9	1	-9	23.7	26.8
9	1	-10	8.9	13.0
9	1	-11	24.7	-21.4
9	1	-12	16.2	-18.4
9	1	-13	18.7	10.0
9	1	-14	8.9	-4.1
9	1	-15	30.8	-27.8
9	1	-16	12.9	8.2
9	2	1	7.4	-4.2
9	2	0	6.0	10.3
9	2	-1	16.1	-13.8
9	2	-2	9.3	-16.7
9	2	-3	14.9	16.1
9	2	-4	8.4	13.3
9	2	-5	26.5	-20.4
9	2	-6	10.6	-3.0
9	2	-7	10.7	14.6
9	2	-8	6.1	9.2
9	2	-9	22.5	-14.2
9	2	-10	8.9	13.0
9	2	-11	24.7	-21.4
9	2	-12	16.2	-18.4
9	2	-13	18.7	10.0
9	2	-14	8.9	-4.1
9	2	-15	30.8	-27.8
9	2	-16	12.9	8.2
9	1	6	6.8	9.7
9	1	5	9.7	-5.0
9	1	4	6.5	-2.3
9	1	3	31.3	28.4
9	1	2	14.6	-4.7
9	1	1	23.3	-23.9
9	1	0	13.6	11.2
9	1	-1	15.8	15.9
9	1	-2	15.3	13.8
9	1	-3	11.5	-7.3
9	1	-4	19.5	-19.0
9	1	-5	14.5	18.6
9	1	-6	13.0	11.4
9	1	-7	24.7	-21.8
9	1	-8	3.6	-6.1
9	1	-9	22.5	-14.2
9	1	-10	8.9	13.0
9	1	-11	24.7	-21.4
9	1	-12	16.2	-18.4
9	1	-13	18.7	10.0
9	1	-14	8.9	-4.1
9	1	-15	30.8	-27.8
9	1	-16	12.9	8.2
8	8	4	15.8	-13.6
8	8	3	15.2	-11.8
8	8	2	20.1	13.1
8	8	1	5.9	5.1
8	8	0	18.1	-15.1
8	8	-1	7.5	-6.6
8	8	-2	9.7	13.9
8	8	-3	20.3	18.0
8	8	-4	16.9	-17.0
8	8	-5	25.0	-21.1
8	8	-6	19.1	12.3
8	8	-7	24.5	21.1
8	8	-8	16.1	-17.1
8	8	-9	15.4	-16.2
8	8	-10	6.1	11.5
8	8	-11	10.0	1.4
8	6	8	5.0	-3.3
8	7	6	12.7	-12.1
8	7	5	12.1	-13.0
8	7	4	38.9	37.4
8	7	3	16.9	-25.8
8	7	2	59.7	-62.1
8	7	1	19.7	-12.9
8	7	0	32.0	32.6
8	7	-1	8.6	9.0
8	7	-2	32.0	-31.6
8	7	-3	37.1	38.1
8	7	-4	47.1	-47.8
8	7	-5	12.1	4.0
8	7	-8	50.3	49.0
8	7	-9	18.2	-13.5
8	7	-10	8.6	-10.2
8	7	-11	17.3	-19.0
8	7	-12	32.8	30.9
8	6	7	13.4	-20.5
8	6	6	8.6	-11.1
8	6	3	46.2	-49.4
8	6	2	4.0	-7.3
8	6	1	18.9	21.5
8	6	0	14.8	15.9
8	6	-1	25.3	-26.3
8	6	-2	14.7	-18.0
8	6	-3	37.6	40.7
8	6	-5	70.2	-71.7
8	6	-6	12.5	-17.8
8	6	-7	52.0	50.6
8	6	-8	6.3	-4.7
8	6	-9	24.2	-25.8
8	6	-10	18.0	-16.0
8	6	-12	14.6	8.3
8	6	-13	30.4	-33.8
8	6	-14	11.7	-7.0
8	6	-15	20.2	17.3
8	6	-16	12.2	8.2
8	6	-17	17.7	-14.1
8	5	11	13.2	7.5
8	5	10	17.9	15.1
8	5	9	11.4	3.3
8	5	8	24.2	-21.4
8	5	7	9.3	9.3
8	5	6	24.3	21.8
8	5	5	23.3	-21.3
8	5	4	31.4	-28.0
8	5	3	28.9	27.8
8	5	2	25.7	27.4
8	5	-1	9.1	12.6
8	5	-3	15.2	-15.8
8	5	-4	70.1	-69.1
8	5	-5	34.6	31.6
8	5	-6	81.6	80.4
8	5	-7	22.9	-27.8
8	5	-8	27.3	-22.7
8	5	-9	22.6	22.2
8	5	-10	20.4	19.7
8	5	-11	14.8	11.2
8	5	-12	27.9	-28.4
8	5	-13	19.0	20.4
8	5	-14	9.0	11.1
8	5	-15	24.0	-26.5
8	5	-16	17.3	-16.8
8	4	-17	6.8	7.2
8	4	-16	21.2	-28.5
8	4	-15	9.3	10.6
8	4	-13	41.2	40.8
8	4	-12	43.0	-46.2
8	4	-11	55.5	60.3
8	4	-10	33.8	-37.8
8	4	-9	52.5	52.2
8	4	-8	30.5	-34.0
8	4	-7	74.7	80.6
8	4	-6	69.6	-71.7
8	4	-5	59.5	61.4
8	4	-4	22.2	-20.4
8	4	-3	25.8	22.8
8	4	-2	93.5	-93.8
8	4	-1	40.9	43.8
8	4	0	4.3	-15.1
8	4	1	9.1	-10.6
8	4	2	7.4	-4.2
8	4	3	6.0	10.3
8	4	4	16.1	-13.8
8	4	5	27.1	32.5
8	4	6	5.5	-6.9
8	4	7	3.3	11.9
8	4	8	9.3	7.2
8	4	9	10.7	14.6
8	4	10	6.1	9.2
8	4	11	22.5	-14.2
8	4	12	3.6	-6.1
8	4	13	6.0	4.6
8	4	14	9.7	6.8
8	4	15	9.7	-5.0
8	4	16	6.5	-2.3
8	3	13	31.3	28.4
8	3	12	14.6	-4.7
8	3	11	23.3	-23.9
8	3	10	13.6	11.2
8	3	9	15.8	15.9
8	3	8	13.6	13.8
8	3	7	19.5	-19.0
8	3	6	14.5	18.6
8	3	5	13.0	11.4
8	3	4	24.7	-21.8
8	3	3	3.6	-6.1
8	3	2	6.0	4.6
8	3	1	9.7	-5.0
8	3	0	6.5	-2.3
8	3	-1	14.1	-15.6
8	3	-2	15.4	-15.2
8	3	-3	17.8	12.9
8	3	-4	19.6	19.7
8	3	-5	31.9	-33.5
8	3	-6	10.4	-12.4
8	3	-7	34.6	34.6
8	3	-8	10.4	-12.4
8	3	-9	31.4	34.6
8	3	-10	19.6	-15.7
8	3	-11	19.6	18.5
8	3	-12	22.5	-20.1
8	3	-13	12.6	10.7
8	3	-14	21.6	16.2
8	3	-15	14.0	-9.6
8	3	-16	16.1	-8.6
8	2	12	12.8	8.2
8	2	11	17.5	19.7
8	2	10	19.3	19.8
8	2	9	54.5	-61.2
8	2	8	60.8	63.4
8	2	7	30.4	-34.4
8	2	6	48.5	52.2
8	2	5	63.3	-64.4
8	2	4	52.2	50.3
8	2	3	39.4	42.2
8	2	2	42.9	-42.9
8	2	1	39.4	42.2
8	2	0	29.8	-29.2
8	1	14	25.8	22.8
8	1	13	93.5	-93.8
8	1	12	40.9	43.8
8	1	11	9.0	10.3
8	1	10	46.2	-49.4
8	1	9	4.0	-7.3
8	1	8	18.9	21.5
8	1	7	14.8	15.9
8	1	6	25.3	-26.3
8	1	5	14.7	-18.0
8	1	4	37.6	40.7
8	1	3	12.5	-17.8
8	1	2	52.0	50.6
8	1	1	6.3	-4.7
8	1	0	24.2	-25.8
8	1	-1	18.0	-16.0
8	1	-2	32.1	32.6
8	1	-3	14.6	8.3
8	1	-4	30.4	-33.8
8	1	-5	11.7	-7.0
8	1	-6	20.2	17.3
8	1	-7	12.2	8.2
8	1	-8	17.7	-14.1
8	1	-9	13.2	7.5
8	1	-10	17.9	15.1
8	1	-11	11.4	3.3
8	1	-12	24.2	-21.4
8	1	-13	9.3	9.3
8	1	-14	11.7	-7.0
8	1	-15	20.2	17.3
8	1	-16	12.2	8.2
8	1	-17	17.7	-14.1
8	0	-15	25.5	21.7
8	0	-14	93.5	-93.8
8	0	-13	40.9	43.8
8	0	-12	25.8	22.8
8	0	-11	93.5	-93.8
8	0	-10	40.9	43.8
8	0	-9	25.8	22.8
8	0	-8	93.5	-93.8
8	0	-7	40.9	43.8
8	0	-6	25.8	22.8
8	0	-5	93.5	-93.8
8	0	-4	40.9	43.8
8	0	-3	25.8	22.8
8	0	-2	93.5	-93.8
8	0	-1	40.9	43.8
8	0	0	25.8	22.8
8	0	1	93.5	-93.8
8	0	2	40.9	43.8
8	0	3	25.8	22.8
8	0	4	93.5	-93.8
8	0	5	40.9	43.8
8	0	6	25.8	22.8
8	0	7	93.5	-93.8
8	0	8	40.9	43.8
8	0	9	25.8	22.8
8	0	10	93.5	-93.8
8	0	11	40.9	43.8
8	0	12	25.8	22.8
8	0	13	93.5	-93.8
8	0	14	40.9	43.8
8	0	15	25.8	22.8
8	0	16	93.5	-93.8
8	0	17	40.9	43.8
8	0	18	25.8	22.8
8	0	19	93.5	-93.8
8	0	20	40.9	43.8
8	0	21	25.8	22.8
8	0	22	93.5	-93.8
8	0	23	40.9	43.8
8	0	24	25.8	22.8
8	0	25	93.5	-93.8
8	0	26	40.9	43.8
8	0	27	25.8	22.8
8	0	28	93.5	-93.8
8	0	29	40.9	43.8
8	0	30	25.8	22.8
8	0	31	93.5	-93.8
8	0	32	40.9	43.8
8	0	33	25.8	22.8
8	0	34	93.5	-93.8
8	0	35	40.9	43.8
8	0	36	25.8	22.8
8	0	37	93.5	-93.8
8	0	38	40.9	43.8
8	0	39	25.8	22.8
8	0	40	93.5	-93.8
8	0	41	40.9	43.8
8	0	42	25.8	22.8
8	0	43	93.5	-93.8
8	0	44	40.9	43.8
8	0	45	25.8	22.8
8	0	46	93.5	-93.8
8	0	47	40.9	43.8
8	0	48	25.8	22.8
8	0	49	93.5	-93.8
8	0	50	40.9	43.8
8	0	51	25.8	22.8
8	0	52	93.5	-93.8
8	0	53	40.9	43.8
8	0	54	25.8	22.8
8	0	55	93.5	-93.8
8	0	56	40.9	43.8
8	0	57	25.8	22.8
8	0	58	93.5	-93.8
8	0	59	40.9	43.8
8	0	60	25.8	22.8
8	0	61	93.5	-93.8
8	0	62	40.9	43.8
8	0	63	25.8	22.8
8	0	64	93.5	-93.8
8	0	65	40.9	43.8
8	0	66	25.8	22.8
8	0	67	93.5	-93.8
8	0	68	40.9	43.8
8	0	69	25.8	22.8
8	0	70	93.5	-93.8
8	0	71	40.9	43.8
8	0	72	25.8	22

H	K	L	F OBS	F CALC
5	5	-9	3.4	1.4
5	5	-10	33.0	-30.9
5	5	-11	24.9	-23.7
5	5	-12	27.0	29.1
5	5	-13	6.2	-8.1
5	5	-14	34.9	-36.9
5	5	-15	8.2	3.7
5	5	-16	23.3	19.2
5	5	-17	10.1	-5.6
5	5	-18	10.6	11.7
5	3	13	13.7	8.8
5	3	12	13.4	-13.0
5	3	11	16.3	21.2
5	3	10	16.3	21.2
5	3	9	9.3	-3.9
5	3	8	5.7	-9.1
5	3	6	6.4	9.3
5	3	5	8.4	8.0
5	3	3	14.9	9.6
5	3	2	97.7	90.4
5	3	1	94.3	93.2
5	3	0	62.4	-65.0
5	3	-2	56.7	54.2
5	3	-3	20.8	-16.2
5	3	-4	19.6	-20.5
5	3	-5	24.5	-26.1
5	3	-6	53.5	57.8
5	3	-7	21.8	21.1
5	3	-8	31.0	-28.8
5	3	-10	19.4	-19.7
5	3	-12	19.0	-14.4
5	3	-13	13.5	-9.1
5	3	-14	22.9	26.5
5	3	-15	22.7	18.9
5	3	-16	14.7	-18.9
5	3	-17	61.6	63.7
5	3	-18	70.6	72.0
5	1	2	30.8	-31.0
5	1	1	121.6	-123.3
5	1	0	21.9	-21.0
5	1	-1	89.7	87.1
5	1	-2	64.0	-67.5
5	1	-3	31.4	-32.5
5	1	-4	6.6	-10.2
5	1	-5	44.8	48.3
5	1	-6	27.4	-24.8
5	1	-7	82.9	-79.3
5	1	-8	54.4	57.1
5	1	-9	66.0	69.9
5	1	-10	59.2	-56.1
5	1	-11	67.9	-68.6
5	1	-12	22.6	21.0
5	1	-13	23.9	24.1
4	6	-16	3.5	-2.3
4	4	13	12.2	12.0
4	4	12	14.8	9.6
4	4	11	11.6	-14.3
4	4	9	39.5	39.7
4	4	8	19.0	19.1
4	4	7	31.1	-30.7
4	4	6	29.9	-34.0
4	4	5	31.4	30.7
4	4	4	23.9	23.1
4	4	3	75.2	-74.2
4	4	2	7.1	10.7
4	4	1	103.6	106.5
4	4	0	33.1	38.2
4	4	-1	54.0	-57.1
4	4	-2	18.1	13.9
4	4	-3	40.2	50.7
4	4	-4	23.2	21.6
4	4	-5	58.7	-58.9
4	4	-6	10.0	-10.1
4	4	-7	31.7	30.7
4	4	-8	38.9	43.3
4	4	-9	69.4	-69.6
4	4	-10	21.9	-25.1
4	4	-11	23.6	20.4
4	4	-12	12.8	11.2
4	4	-13	27.0	-27.1
4	4	-14	27.8	27.0
4	4	-15	6.2	4.9
4	4	-17	21.2	-21.5
4	4	-18	15.4	-2.2
4	2	15	16.3	-3.6
4	2	14	9.2	8.8
4	2	13	12.2	-15.9
4	2	12	20.2	-18.1
4	2	11	23.5	21.7
4	2	10	17.1	20.1
4	2	9	12.4	-17.0
4	2	8	19.9	-18.8
4	2	7	16.7	-13.4
4	2	6	28.5	23.9
4	2	5	14.6	-15.5
4	2	4	64.2	-64.9
4	2	3	62.7	62.6
4	2	2	141.3	132.9
4	2	1	19.3	-19.8
4	2	0	136.0	-133.7
4	2	-1	12.0	-10.3
4	2	-2	10.7	11.5
4	2	-3	38.6	33.6
4	2	-4	60.2	-56.7
4	2	-5	13.6	12.8
4	2	-6	66.0	65.1
4	2	-7	75.4	-80.3
4	2	-8	37.3	-35.7
4	2	-9	87.4	23.6
4	2	-10	65.8	69.1
4	2	-11	14.8	9.4
4	2	-12	23.7	-23.6
4	2	-13	14.7	16.7
3	7	-12	9.3	-4.0
3	7	-13	11.2	4.4
3	7	-14	15.2	11.4
3	5	14	13.1	-11.5
3	5	13	13.4	-8.3
3	5	12	8.0	8.9
3	5	11	6.7	3.1
3	5	10	36.0	-34.8
3	5	8	80.2	46.0
3	5	7	20.5	21.8
3	5	6	81.5	-30.8
3	5	5	1.8	-3.5
3	5	4	24.5	21.1
3	5	3	7.7	-4.0
3	5	2	47.7	-46.0
3	5	1	7.2	8.0
3	5	0	90.1	92.0
3	5	-1	32.2	-33.4
3	5	-2	75.0	-73.7
3	5	-3	7.1	2.5
3	5	-4	28.0	30.0
3	5	-5	43.3	47.4
3	5	-6	64.7	-64.9
3	5	-7	19.8	-19.9
3	5	-8	86.6	85.9
3	5	-9	16.0	-13.0
3	5	-10	46.6	-49.8
3	5	-11	5.8	1.8
3	5	-12	9.0	6.5
3	5	-14	12.8	-19.8
3	5	-15	14.9	-15.9
3	5	-16	11.5	-9.6
3	5	-17	7.7	6.2
3	3	14	14.0	7.3
3	3	13	11.8	-9.6
3	3	12	15.4	-13.1
3	3	11	19.8	-6.6
3	3	10	83.1	25.3
3	3	9	46.3	44.7
3	3	8	14.9	-15.9
3	3	7	11.5	-9.6
3	3	6	89.9	29.8
3	3	5	85.7	62.2
3	3	4	79.9	-77.0
3	3	3	8.9	11.5
3	3	2	114.3	105.6
3	3	1	80.1	25.3
3	3	0	36.1	-38.7
3	3	-1	86.0	-93.1
3	3	-2	69.0	61.6
3	3	-5	18.7	19.1
3	3	-6	92.9	92.8
3	3	-7	28.2	26.7
3	3	-8	46.2	-47.4
3	3	-9	30.3	-31.0
3	3	-11	27.8	28.5
3	3	-12	11.2	-8.1
3	3	-13	15.8	13.2
3	3	-14	36.0	33.8
3	3	-15	9.0	15.6
2	8	2	42.4	40.8
2	8	1	12.7	7.5
2	8	0	31.1	-29.3
2	8	-1	12.9	-13.3
2	8	-2	14.2	13.6
2	8	-3	19.4	20.4
2	8	-4	10.8	-10.2
2	8	-5	17.9	-22.8
2	8	-6	19.1	18.4
2	8	-7	14.1	14.8
2	8	-8	27.8	-29.8
2	8	-9	7.9	-14.4
2	8	-10	21.8	21.9
2	8	-11	6.7	1.4
2	8	-12	13.2	-4.1
2	8	-13	20.2	-21.0
2	6	13	9.4	-12.2
2	6	12	20.7	10.5
2	6	11	25.7	22.0
2	6	10	14.4	-13.2
2	6	9	37.3	-40.0
2	6	8	3.6	4.1
2	6	7	26.6	24.5
2	6	5	15.8	-4.9
2	6	4	6.4	2.6
2	6	3	43.8	44.0
2	6	2	19.8	-16.9
2	6	1	39.1	-41.4
2	6	0	31.7	31.1
2	6	-1	41.5	42.5
2	6	-2	21.9	-19.2
2	6	-3	44.3	-49.7
2	6	-4	26.1	-28.0
2	6	-5	47.3	52.1
2	6	-6	12.6	-6.6
2	6	-7	41.5	-43.2
2	6	-8	15.9	13.4
2	6	-9	45.3	46.7
2	4	-10	12.8	-15.8
2	4	-11	9.6	-7.0
2	4	-12	5.0	-7.7
2	4	-13	14.1	12.8
2	4	-14	2.6	6.5
2	4	-15	18.5	-17.7
2	4	-16	9.1	6.1
2	4	15	14.3	-11.1
2	4	13	16.3	21.3
2	4	12	20.1	17.7
2	4	11	26.7	-28.0
2	4	10	15.8	-22.3
2	4	9	51.9	55.4
2	4	8	25.6	23.3
2	4	7	52.4	-55.5
2	4	5	76.9	80.4
2	4	4	18.9	14.1
2	4	3	62.9	-64.1
2	4	2	19.6	22.1
2	4	1	103.9	101.0
2	4	0	45.5	49.6
2	4	-1	117.4	-117.0
2	4	-2	38.6	-39.4
2	4	-3	43.6	42.6
2	4	-4	72.2	72.1
2	4	-5	27.5	-28.0
2	4	-6	33.2	-40.6
2	4	-7	93.1	97.1
2	4	-8	20.5	18.8
2	4	-9	54.4	-57.5
2	4	-10	7.2	-10.1
2	4	-11	39.9	39.6
2	4	-13	20.7	-25.3
2	4	-14	11.4	4.8
2	4	-15	22.9	20.0
2	4	-16	14.1	16.5
2	4	-17	11.0	-21.3
2	2	16	11.2	-12.0
2	2	14	9.0	-2.6
2	2	12	20.3	-21.2
2	2	11	21.7	15.9
2	2	10	17.2	13.7
2	2	9	44.6	-43.5
2	2	8	52.0	-54.5
2	2	7	28.3	30.4
2	2	6	71.5	74.7
2	2	5	9.6	-8.9
2	2	4	91.1	-88.6
2	2	3	45.6	44.4
2	2	2	33.2	-24.5
2	2	1	98.5	-79.6
2	2	0	171.3	-161.1
2	2	-1	49.0	-37.3
2	2	-2	8.9	2.1
2	2	-3	131.2	-126.8
2	2	-5	58.0	57.1
2	2	-6	83.7	81.5
2	2	-7	40.3	-44.5
2	2	-8	46.9	-51.4
2	0	-3	23.3	21.4
2	0	-10	35.4	36.2
2	2	-11	7.0	0.7
2	2	-12	39.6	-39.9
2	2	-13	10.6	10.5
2	2	-14	16.5	16.1
2	2	-15	17.4	-20.7
2	2	-16	25.2	-24.7
2	2	-18	16.9	13.9
2	0	16	37.0	35.3
2	0	14	13.7	-11.7
2	0	12	55.2	53.6
2	0	10	63.8	-66.9
2	0	8	116.3	122.3
2	0	6	61.7	-60.0
2	0	4	100.3	94.7
2	0	2	113.4	-115.1
2	0	0	169.6	172.3
2	0	-2	110.1	-114.9
2	0	-4	325.9	327.4
2	0	-6	195.7	-193.6
2	0	-8	74.2	72.0
2	0	-10	31.8	-35.6
2	0	-12	25.0	22.9
2	0	-14	40.4	-40.7
2	0	-16	33.6	35.9
2	0	-18	20.6	-18.2
1	11	2	5.1	-3.1
1	11	1	15.5	-14.2
1	11	-1	14.2	15.9
1	11	-3	16.2	-12.5
1	9	10	9.1	-5.9
1	9	8	4.2	9.2
1	9	7	29.1	-24.8
1	9	6	4.0	-6.0
1	9	5	24.2	21.2
1	9	3	22.5	-26.9
1	9	2	15.5	-8.5
1	9	1	34.8	38.1
1	9	0	10.3	-1.6
1	9	-1	26.1	-24.4
1	9	-2	19.8	-22.6
1	9	-3	12.9	15.2
1	9	-4	10.5	8.8
1	9	-5	19.9	-21.2
1	9	-6	31.0	27.4
1	9	-7	29.8	30.2
1	9	-8	4.7	-2.3
1	9	-9	24.4	-26.0
1	7	13	12.4	-11.8
1	7	11	10.9	14.9
1	7	10	33.1	33.7
1	7	9	11.0	-5.8
1	7	8	33.3	-31.7
1	7	7	9.8	-1.7
1	7	6	31.0	27.4
1	7	5	8.7	-14.4
1	7	4	30.3	-26.0
1	7	3	30.1	31.7
1	7	2	42.6	43.5
1	7	1	28.6	-31.4
1	7	0	22.2	-25.9
1	7	-1	18.3	22.4
1	7	-2	53.0	53.5
1	7	-3	19.7	-20.7
1	7	-4	21.4	-24.0
1	7	-5	25.3	24.6
1	7	-6	30.2	-30.4
1	7	-8	30.8	-29.0
1	7	-9	16.2	17.3
1	7	-10	17.8	21.8
1	5	13	3.9	-0.8
1	5	12	23.5	26.7
1	5	11	22.3	23.1
1	5	10	30.7	-27.3
1	5	9	9.6	-4.9
1	5	8	32.9	29.5
1	5	6	13.3	-8.1
1	5	5	24.4	-23.3
1	5	4	27.8	30.4
1	5	3	9.7	-13.1
1	5	2	62.9	-61.9
1	5	1	20.2	-17.9
1	5	0	80.3	80.4
1	5	-1	72.6	72.1
1	5	-2	85.2	-86.1
1	5	-3	42.1	-43.8
1	5	-4	41.4	42.0
1	5	-5	25.2	23.2
1	5	-6	87.2	-89.2
1	5	-8	32.8	35.8
1	5	-9	8.8	-4.2
1	5	-10	24.5	-25.8
1	5	-11	14.7	-19.3
1	5	-14	80.7	17.2
1	3	17	11.6	-0.5
1	3	14	12.9	-10.3
1	3	14	20.7	9.8
1	3	13	9.4	15.0
1	3	12	10.7	-8.6
1	3	11	19.9	-21.0
1	3	10	34.1	34.4
1	3	9	19.1	20.8
1	3	8	94.4	-88.2
1	3	7	20.3	-35.4
1	3	6	89.2	36.0
1	3	5	16.8	17.3
1	3	4	87.8	-35.6
1	3	3	15.8	-19.7
1	3	2	70.0	71.2
1	3	1	25.7	32.7
1	3	0	61.9	-70.4
1	3	-1	11.9	-13.3
1	3	-2	38.4	29.6
1	3	-3	15.8	16.9
1	3	-4	21.3	-25.0
1	3	-5	39.2	-40.1
1	3	-6	42.7	41.9
1	3	-8	28.1	27.4
1	3	-9	60.3	-59.4
1	3	-10	45.2	48.9
1	3	-11	40.5	44.1
1	3	-12	26.0	-26.6
1	3	-14	16.5	19.5
1	3	-16	11.0	-7.8
1	3	-17	13.2	-12.5
1	1	18	13.4	12.6
1	1	19	14.6	-16.9
1	1	16	11.8	8.7
1	1	15	12.2	13.8
1	1	14	18.2	11.2
1	1	13	12.3	3.8
1	1	12	10.5	-5.2
1	1	11	14.4	19.5
1	1	10	10.3	-9.4
1	1	9	89.7	-61.4
1	1	8	84.1	-24.5
1	1	7	81.8	53.2
1	1	6	85.5	55.1
1	1	5	8.9	-14.8
1	1	4	97.6	-97.6
1	1	3	84.7	-89.6
1	1	2	94.7	97.7
1	1	1	158.7	-155.5
1	1	0	63.2	64.5
1	1	-1	149.6	149.8
1	1	-2	37.4	-42.4
1	1	-3	83.7	-87.7
1	1	-4	90.1	-29.0
1	1	-5	10.2	5.0
1	1	-6	24.4	6.6
1	1	-7	17.7	17.8
1	1	-8	82.9	-93.6
1	1	-9	17.7	19.1
1	1	-10	18.3	16.9
1	1	-11	48.4	-51.9
1	1	-12	24.2	-24.3
1	1	-13	11.4	11.3
1	1	-14	12.9	-11.0
1	1	-15	32.0	-29.9
1	1	-16	14.4	12.9
1	1	-17	10.1	12.4
1	1	-18	9.9	-1.9
0	10	8	17.7	17.8
0	10	6	13.0	-14.2
0	10	5	10.0	-4.6
0	10	4	11.7	12.7
0	10	3	13.8	16.6
0	10	2	21.3	-19.2
0	10	1	32.0	31.2
0	10	0	20.7	23.8
0	8	12	9.6	-4.9
0	8	10	14.5	11.1
0	8	9	26.9	24.0
0	8	8	17.1	-17.2
0	8	7	15.8	-12.1
0	8	6	20.3	18.8
0	8	5	8.5	2.0
0	8	4	12.8	-12.0
0	8	3	17.0	-14.9
0	8	2	17.4	9.9
0	8	1	22.0	22.8
0	8	0	25.0	-25.1
0	6	15	20.6	13.3
0	6	14	10.8	-9.7
0	6	13	18.6	-20.3
0	6	12	13.0	13.1
0	6	11	18.2	18.2
0	6	10	8.5	3.9
0	6	9	24.1	-21.9
0	6	8	14.6	14.9
0	6	7	25.3	24.3
0	6	6	25.5	25.1
0	6	5	15.6	-17.0
0	6	4	40.0	36.4
0	6	3	41.0	39.2
0	6	2	89.6	-27.0
0	6	1	90.2	-72.9
0	4	17	13.9	12.4
0	4	16	7.3	9.0
0	4	15	16.8	-20.3
0	4	14	12.2	-10.7
0	4	13	24.8	27.0
0	4	12	29.6	27.6
0	4	11	38.0	-39.6
0	4	10	11.8	-4.8
0	4	9	67.8	70.0
0	4	8	9.3	-5.9
0	4	7	71.5	-70.3
0	4	6	1.6	-0.6
0	4	5	44.4	46.4
0	4	4	82.4	32.5
0	4	3	180.1	-128.9
0	4	2	48.3	-43.0
0	4	1	90.0	63.1
0	4	0	86.4	91.8
0	2	18	6.2	6.9
0	2	17	11.2	-11.2
0	2	16	15.9	-15.8
0	2	15	19.7	14.9
0	2	14	5.3	0.9
0	2	12	35.1	-36.6
0	2	11	28.0	29.6
0	2	10	43.2	46.4
0	2	9	92.4	-92.0
0	2	8	69.9	-70.1
0	2	7	49.4	52.2
0	2	5	12.2	5.4
0	2	4	74.2	-76.9
0	2	3	7.0	-6.1
0	2	2	10.1	-12.7
0	2	1	202.9	-200.9
0	2	0	87.0	-83.5
0	0	18	17.4	-22.1
0	0	16	6.1	3.1
0	0	14	10.9	-20.7
0	0	12	84.5	65.6
0	0	10	92.6	-86.3
0	0	8	114.2	121.6
0	0	6	80.8	-73.0
0	0	4	91.4	88.5
0	0	2	141.5	-153.3

TABLE 16

$Cu(py)_3(NO_3)_2$

Observed and final-calculated structure amplitudes

H	K	L	F OBS	F CALC
15	1	-7	1.8	-43
15	1	-6	4.4	4.0
15	1	-5	14.1	-13.6
15	1	-4	6.5	-7.8
14	2	1	12.9	12.7
14	2	0	7.4	-7.3
14	2	-1	5.8	6.1
14	2	-2	20.9	21.8
14	2	-3	7.2	-5.9
14	2	-4	17.2	16.7
14	2	-5	12.7	7.9
14	2	-6	14.8	13.3
14	2	-7	5.6	-4.5
14	2	-8	11.1	-9.3
14	2	-9	11.5	12.0
14	2	-10	11.2	14.9
14	2	-11	11.2	11.6
14	2	-12	11.2	11.6
14	0	6	18.4	17.6
14	0	2	10.3	11.2
14	0	-2	10.3	9.2
14	0	-4	6.5	9.2
14	0	-6	29.3	26.5
14	0	-8	10.8	9.7
14	0	-10	30.5	32.4
14	0	-12	27.5	24.4
13	3	1	12.5	11.8
13	3	0	7.4	8.0
13	3	-1	14.5	13.9
13	3	-2	19.9	17.4
13	3	-3	11.2	11.7
13	3	-4	26.8	27.2
13	3	-5	10.7	2.4
13	3	-6	22.1	14.4
13	3	-7	7.8	10.1
13	3	-8	11.5	10.5
13	3	-10	12.8	11.2
13	3	-11	11.5	6.6
13	3	-12	12.5	9.3
13	3	-13	12.1	8.4
13	1	4	7.2	8.3
13	1	2	12.2	11.5
13	1	1	8.7	5.1
13	1	0	16.3	13.3
13	1	-1	8.1	9.2
13	1	-2	9.1	9.2
13	1	-3	6.4	9.0
13	1	-4	39.6	40.6
13	1	-5	4.3	1.7
13	1	-6	34.2	32.4
13	1	-7	7.8	8.4
13	1	-8	4.3	3.7
13	1	-9	37.8	33.7
13	1	-10	4.6	1.2
13	1	-11	5.9	10.1
13	1	-12	10.6	10.9
13	1	-13	35.6	34.5
13	1	-14	4.4	5.3
13	1	-15	22.1	22.6
13	1	-16	14.3	14.0
13	1	-17	4.7	3.6
13	1	-18	9.2	9.2
12	4	0	12.2	11.0
12	4	-1	9.4	9.6
12	4	-2	7.8	7.9
12	4	-3	23.7	24.6
12	4	-4	6.5	7.9
12	4	-5	21.0	17.9
12	4	-6	10.2	2.1
12	4	-7	16.3	20.2
12	4	-8	13.7	13.7
12	4	-9	10.7	14.7
12	4	-10	16.3	13.9
12	4	-11	20.4	20.4
12	4	-12	8.2	8.6
12	4	-13	27.3	23.9
12	4	-14	8.3	8.7
12	4	-15	23.0	22.0
12	4	-16	8.2	9.6
12	4	-17	23.9	23.9
12	4	-18	9.2	9.2
12	4	-19	11.4	11.4
12	4	-20	9.2	9.2
12	2	5	14.4	-13.2
12	2	4	13.5	-13.6
12	2	3	23.0	17.4
12	2	2	14.3	13.5
12	2	1	11.5	-11.9
12	2	0	21.7	21.6
12	2	-1	9.2	-9.2
12	2	-2	9.2	8.2
12	2	-3	23.6	-23.0
12	2	-4	15.6	-20.4
12	2	-5	31.7	30.6
12	2	-6	22.7	25.3
12	2	-7	22.1	23.1
12	2	-8	17.6	15.4
12	2	-9	9.7	12.6
12	2	-10	13.3	12.6
12	2	-11	14.7	-14.6
12	2	-12	17.8	14.4
12	2	-13	20.4	14.4
12	2	-14	15.5	19.3
12	2	-15	13.2	-14.5
12	0	6	10.7	-10.4
12	0	4	45.4	37.7
12	0	2	19.1	-13.6
12	0	0	11.7	4.7
12	0	-2	34.8	-32.2
12	0	-4	44.5	45.5
12	0	-6	70.1	-84.9
12	0	-8	31.5	23.4
12	0	-10	23.4	-26.4
12	0	-12	39.9	34.2
12	0	-14	35.1	34.7
11	7	-5	15.1	13.7
11	7	-6	16.6	-14.0
11	7	-7	16.5	-14.6
11	7	-8	17.0	-15.0
11	7	-9	10.6	10.6
11	5	4	11.2	11.1
11	5	2	10.9	11.1
11	5	0	70.5	13.4
11	5	-1	11.2	9.6
11	5	-2	20.1	-12.9
11	5	-3	9.9	-9.1
11	5	-4	29.3	21.3
11	5	-5	1.2	4.7
11	5	-6	23.9	-20.7
11	5	-7	12.9	-9.3
11	5	-8	21.9	21.0
11	5	-10	15.2	-12.4
11	5	-12	6.7	9.3
11	3	7	11.4	-9.1
11	3	6	18.0	18.3
11	3	5	12.5	12.6
11	3	4	7.9	-5.9
11	3	3	24.9	19.6
11	3	2	16.9	14.7
11	3	1	16.9	14.8
11	3	0	14.8	9.1
11	3	-1	8.5	-8.0
11	3	-2	22.2	16.1
11	3	-3	11.6	9.6
11	3	-4	39.5	-39.8
11	3	-5	18.0	-16.6
11	3	-6	15.6	16.5
11	3	-7	11.9	9.3
11	3	-8	14.7	-12.8
11	3	-9	11.6	-9.6
11	3	-10	20.5	17.3
11	3	-11	19.0	17.9
11	3	-12	30.4	25.3
11	3	-13	14.4	-15.7
11	3	-14	25.4	24.7
11	3	-15	17.8	14.3
11	1	8	10.1	1.0
11	1	7	11.8	9.9
11	1	6	25.9	-20.4
11	1	5	3.7	-3.2
11	1	3	13.8	12.0
11	1	2	14.7	15.0
11	1	1	10.1	-9.4
11	1	0	9.8	-8.2
11	1	-1	18.6	-9.2
11	1	-2	4.7	-7.1
11	1	-3	39.6	-40.6
11	1	-4	4.3	1.7
11	1	-5	34.2	32.4
11	1	-6	4.3	3.7
11	1	-7	37.8	-33.7
11	1	-8	4.6	1.2
11	1	-9	5.9	-10.1
11	1	-10	10.6	10.9
11	1	-11	35.6	-34.5
11	1	-12	4.4	5.3
11	1	-13	25.9	22.6
11	1	-14	14.3	14.0
11	1	-15	4.7	3.6
11	1	-16	9.2	9.2
10	8	1	9.7	-9.6
10	8	-1	7.2	8.7
10	8	-3	6.0	9.4
10	8	-4	16.4	-17.0
10	8	-5	14.7	12.6
10	8	-7	4.9	6.6
10	6	4	14.7	15.6
10	6	3	16.9	13.8
10	6	1	17.2	-14.3
10	6	-1	20.4	-20.3
10	6	-2	8.6	-8.3
10	6	-3	28.1	-27.4
10	6	-4	28.4	29.6
10	6	-5	31.0	29.5
10	6	-6	18.1	-19.5
10	6	-7	18.7	19.7
10	6	-8	19.2	4.2
10	6	-10	12.7	10.7
10	6	-11	12.7	-8.2
10	6	-12	10.4	10.2
10	6	-13	16.2	19.2
10	4	7	12.4	-12.5
10	4	6	9.2	-8.7
10	4	5	42.4	-39.5
10	4	4	2.7	2.5
10	4	3	42.4	-39.5
10	4	2	10.8	29.8
10	4	1	15.4	15.3
10	4	0	15.4	13.0
10	4	-1	5.1	7.2
10	4	-2	29.1	-26.8
10	4	-3	9.7	-11.6
10	4	-4	39.1	40.0
10	4	-5	20.7	20.7
10	4	-6	47.4	-40.2
10	4	-7	20.7	-20.1
10	4	-8	30.7	33.1
10	4	-9	8.4	-7.9
10	4	-10	31.0	-29.9
10	4	-11	12.3	-12.5
10	4	-12	30.9	28.0
10	4	-13	11.4	10.4
10	4	-14	33.7	-32.4
10	4	-15	8.2	-8.2
10	4	-16	33.0	30.4
10	2	7	10.9	-8.9
10	2	6	11.8	11.9
10	2	5	8.3	8.7
10	2	4	35.9	-33.5
10	2	3	19.7	18.3
10	2	2	6.6	6.1
10	2	1	29.3	-29.2
10	2	0	21.4	-17.3
10	2	-1	29.0	29.8
10	2	-2	23.1	21.8
10	2	-3	30.2	-27.8
10	2	-4	22.3	-22.2
10	2	-5	18.3	17.6
10	2	-6	20.7	20.6
10	2	-7	10.9	-10.4
10	2	-8	22.1	19.7
10	2	-9	11.8	11.9
10	2	-10	8.3	8.7
10	2	-11	35.9	-33.5
10	2	-12	19.7	18.3
10	2	-13	6.6	6.1
10	2	-14	29.3	-29.2
10	2	-15	21.4	-17.3
10	2	-16	29.0	29.8
10	2	-17	23.1	21.8
10	2	-18	30.2	-27.8
10	2	-19	22.3	-22.2
10	2	-20	18.3	17.6
10	2	-21	20.7	20.6
10	2	-22	10.9	-10.4
10	2	-23	22.1	19.7
10	2	-24	11.8	11.9
10	2	-25	8.3	8.7
10	2	-26	35.9	-33.5
10	2	-27	19.7	18.3
10	2	-28	6.6	6.1
10	2	-29	29.3	-29.2
10	2	-30	21.4	-17.3
10	2	-31	29.0	29.8
10	2	-32	23.1	21.8
10	2	-33	30.2	-27.8
10	2	-34	22.3	-22.2
10	2	-35	18.3	17.6
10	2	-36	20.7	20.6
10	2	-37	10.9	-10.4
10	2	-38	22.1	19.7
10	2	-39	11.8	11.9
10	2	-40	8.3	8.7
10	2	-41	35.9	-33.5
10	2	-42	19.7	18.3
10	2	-43	6.6	6.1
10	2	-44	29.3	-29.2
10	2	-45	21.4	-17.3
10	2	-46	29.0	29.8
10	2	-47	23.1	21.8
10	2	-48	30.2	-27.8
10	2	-49	22.3	-22.2
10	2	-50	18.3	17.6
10	2	-51	20.7	20.6
10	2	-52	10.9	-10.4
10	2	-53	22.1	19.7
10	2	-54	11.8	11.9
10	2	-55	8.3	8.7
10	2	-56	35.9	-33.5
10	2	-57	19.7	18.3
10	2	-58	6.6	6.1
10	2	-59	29.3	-29.2
10	2	-60	21.4	-17.3
10	2	-61	29.0	29.8
10	2	-62	23.1	21.8
10	2	-63	30.2	-27.8
10	2	-64	22.3	-22.2
10	2	-65	18.3	17.6
10	2	-66	20.7	20.6
10	2	-67	10.9	-10.4
10	2	-68	22.1	19.7
10	2	-69	11.8	11.9
10	2	-70	8.3	8.7
10	2	-71	35.9	-33.5
10	2	-72	19.7	18.3
10	2	-73	6.6	6.1
10	2	-74	29.3	-29.2
10	2	-75	21.4	-17.3
10	2	-76	29.0	29.8
10	2	-77	23.1	21.8
10	2	-78	30.2	-27.8
10	2	-79	22.3	-22.2
10	2	-80	18.3	17.6
10	2	-81	20.7	20.6
10	2	-82	10.9	-10.4
10	2	-83	22.1	19.7
10	2	-84	11.8	11.9
10	2	-85	8.3	8.7
10	2	-86	35.9	-33.5
10	2	-87	19.7	18.3
10	2	-88	6.6	6.1
10	2	-89	29.3	-29.2
10	2	-90	21.4	-17.3
10	2	-91	29.0	29.8
10	2	-92	23.1	21.8
10	2	-93	30.2	-27.8
10	2	-94	22.3	-22.2
10	2	-95	18.3	17.6
10	2	-96	20.7	20.6
10	2	-97	10.9	-10.4
10	2	-98	22.1	19.7
10	2	-99	11.8	11.9
10	2	-100	8.3	8.7
10	2	-101	35.9	-33.5
10	2	-102	19.7	18.3
10	2	-103	6.6	6.1
10	2	-104	29.3	-29.2
10	2	-105	21.4	-17.3
10	2	-106	29.0	29.8
10	2	-107	23.1	21.8
10	2	-108	30.2	-27.8
10	2	-109	22.3	-22.2
10	2	-110	18.3	17.6
10	2	-111	20.7	20.6
10	2	-112	10.9	-10.4
10	2	-113	22.1	19.7
10	2	-114	11.8	11.9
10	2	-115	8.3	8.7
10	2	-116	35.9	-33.5
10	2	-117	19.7	18.3
10	2	-118	6.6	6.1
10	2	-119	29.3	-29.2
10	2	-120	21.4	-17.3
10	2	-121	29.0	29.8
10	2	-122	23.1	21.8
10	2	-123	30.2	-27.8
10	2	-124	22.3	-22.2
10	2	-125	18.3	17.6
10	2	-126	20.7	20.6
10	2	-127	10.9	-10.4
10	2	-128	22.1	19.7
10	2	-129	11.8	11.9
10	2	-130	8.3	8.7
10	2	-131	35.9	-33.5
10	2	-132	19.7	18.3
10	2	-133	6.6	6.1
10	2	-134	29.3	-29.2
10	2	-135	21.4	-17.3
10	2	-136	29.0	29.8
10	2	-137	23.1	21.8
10	2	-138	30.2	-27.8
10	2	-139	22.3	-22.2
10	2	-140	18.3	17.6
10	2	-141	20.7	20.6
10	2	-142	10.9	-10.4
10	2	-143	22.1	19.7
10	2	-144	11.8	11.9
10	2	-145	8.3	8.7
10	2	-146	35.9	-33.5
10	2	-147	19.7	18.3
10	2	-148	6.6	6.1
10	2	-149	29.3	-29.2
10	2	-150	21.4	-17.3
10	2	-151	29.0	29.8
10	2	-152	23.1	21.8
10	2	-153	30.2	-27.8
10	2	-154	22.3	-22.2
10	2	-155	18.3	17.6
10	2	-156	20.7	20.6
10	2	-157	10.9	-10.4
10	2	-158	22.1	19.7
10	2	-159	11.8	11.9
10	2	-160	8.3	8.7
10	2	-161	35.9	-33.5
10	2	-162	19.7	18.3
10	2	-163	6.6	6.1
10	2	-164	29.3	-29.2
10	2	-165	21.4	-17.3
10	2	-166	29.0	29.8
10	2	-167	23.1	21.8
10	2	-168	30.2	-27.8
10	2	-169	22.3	-22.2
10	2	-170	18.3	17.6
10	2	-171	20.7	20.6
10	2	-172	10.9	-10.4
10	2	-173	22.1	19.7
10	2	-174	11.8	11.9
10	2	-175	8.3	8.7
10	2	-176	35.9	-33.5
10	2	-177	19.7	18.3
10	2	-178	6.6	6.1
10	2	-179	29.3	-29.2
10	2	-180	21.4	-17.3
10	2	-181	29.0	29.8
10	2	-182	23.1	21.8
10	2	-183	30.2	-27.8
10	2	-184	22.3	-22.2
10	2	-185	18.3	17.6
10	2	-186	20.7	20.6
10	2	-187	10.9	-10.4
10	2	-188	22.1	19.7
10	2	-189	11.8	11.9
10	2	-190	8.3	8.7
10	2	-191	35.9	-33.5
10	2	-192	19.7	18.3
10	2	-193	6.6	6.1
10	2	-194	29.3	-29.2
10	2	-195	21.4	-17.3
10	2	-196	29.0	29.8
10	2	-197	23.1	21.8
10	2	-198	30.2	-27.8
10	2	-199	22.3	-22.2
10	2	-200	18.3	17.6
10	2	-201	20.7	20.6
10	2	-202	10.9	-10.4
10	2	-203	22.1	19.7
10	2	-204	11.8	11.9
10	2	-205	8.3	8.7
10	2	-206	35.9	-33.5
10	2	-207	19.7	18.3
10	2	-208	6.6	6.1
10	2	-209	29.3	-29.2
10	2	-210	21.4	-17.3
10	2	-211	29.0	29.8
10	2	-212	23.1	21.8
10	2	-213	30.2	-27.8
10	2	-214	22.3	-22.2
10	2	-215	18.3	17.6
10	2	-216	20.7	20.6
10	2	-217	10.9	-10.4
10	2	-218	22.1	19.7
10	2	-219	11.8	11.9
10	2	-220	8.3	8.7
10	2	-221	35.9	-33.5
10	2	-222	19.7	18.3
10	2	-223	6.6	6.1
10	2	-224	29.3	-29.2
10	2	-225	21.4	-17.3
10	2	-226	29.0	29.8
10	2	-227	23.1	21.8
10	2	-228	30.2	-27.8
10	2	-229	22.3	-22.2
10	2	-230	18.3	17.6
10	2	-231	20.7	20.6
10	2	-232	10.9	-10.4
10	2	-233	22.1	19.7
10	2	-234	11.8	11.9
10	2	-235	8.3	8.7
10	2	-236	35.9	-33.5
10	2	-237	19.7	18.3
10	2	-238	6.6	6.1
10	2	-239	29.3	-29.2
10	2	-240	21.4	-17.3
10	2	-241	29.0	29.8
10	2	-242	23.1	21.8
10	2	-243	30.2	-27.8
10	2	-244	22.3	-22.2
10	2	-245	18.3	17.6
10	2	-246	20.7	20.6
10	2	-247	10.9	-10.4
10	2	-248	22.1	19.7
10	2	-249	11.8	11.9
10	2	-250	8.3	8.7
10	2	-251	35.9	-33.5
10	2	-252	19.7	18.3
10	2	-253	6.6	6.1
10	2	-254	29.3	-29.2
10	2	-255	21.4	-17.3
10	2	-256	29.0	29.8
10	2	-257	23.1	21.8
10	2	-258	30.2	-27.8
10	2	-259	22.3	-22.2
10	2	-260	18.3	17.6
10	2	-261	20.7	20.6
10	2	-262	10.9	-10.4
10	2	-263	22.1	19.7
10	2	-264	11.8	11.9
10	2	-265	8.3	8.7
10	2	-266	35.9	-33.5
10	2	-267	19.7	18.3
10	2	-268	6.6	6.1
10	2	-269	29.3	-29.2
10	2	-270	21.4	-17.3
10	2	-271	29.0	29.8
10	2	-272	23.1	21.8
10	2	-273	30.2	-27.8
10	2	-274	22.3	-22.2
10	2	-275	18.3	17.6
10	2	-276	20.7	20.6
10	2	-277	10.9	-10.4
10	2	-278	22.1	19.7
10	2	-279	11.8	11.9
10	2	-280	8.3	8.7
10	2	-281	35.9	-33.5
10	2	-282	19.7	18.3
10	2	-283	6.6	6.1
10	2	-284	29.3	-29.2
10	2	-285	21.4	-17.3
10	2	-286	29.0	29.8
10	2	-287	23.1	21.8
10	2	-288	30.2	-27.8
10	2	-289	22.3	-22.2
10	2	-290	18.3	17.6
10	2	-291	20.7	20.6
10	2	-292	10.9	-10.4
10	2	-293	22.1	19.7
10	2	-294	11.8	11.9
10	2	-295	8.3	8.7
10	2	-296	35.9	-33.5
10	2	-297	19.7	18.3
10	2	-298	6.6	6.1
10	2	-299	29.3	-29.2
10	2	-300	21.4	-17.3
10	2	-301	29.0	29.8
10	2	-302	23.1	21.8
10	2	-303	30.2	-27.8
10	2	-304	22.3	-22.2
10	2	-305	18.3	17.6
10	2	-306	20.7	20.6
10	2	-307	10.9	-10.4
10	2	-308	22.1	19.7
10	2	-309	11.8	11.9
10	2	-310	8.3	8.7
10	2	-311	35.9	-33.5
10	2	-312	19.7	18.3
10	2	-313	6.6	6.1
10	2	-314	29.3	-29.2
10	2	-315	21.4	-17.3
10	2	-316	29.0	29.8
10	2	-317	23.1	21.8
10	2	-318	30.2	-27.8
10	2	-319	22.3	-22.2
10	2	-320	18.3	17.6
10	2	-321	20.7	20.6
10	2	-322	10.9	-10.4
10	2	-323	22.1	19.7
10	2	-324	11.8	11.9
10	2	-325	8.3	8.7
10	2	-326	35.9	-33.5
10	2	-327	19.7	18.3
10	2	-328	6.6	6.1
10	2	-329	29.3	-29.2
10	2	-330	21.4	-17.3
10	2	-331	29.0	29.8
10	2	-332	23.1	21.8
10	2	-333	30.2	-27.8
10	2	-334	22.3	-22.2
10	2	-335	18.3	17.6
10	2	-336	20.7	20.6
10	2	-337	10.9	-10.4
10	2	-338	22.1	19.7
10	2	-339	11.8	11.9
10	2	-340	8.3	8.7
10	2	-341	35.9	-33.5
10	2	-342	19.7	18.3
10	2	-343	6.6	6.1
10	2	-344	29.3	-29.2
10	2	-345	21.4	-17.3
10	2	-346	29.0	29.8
10	2	-347	23.1	21.8
10	2	-348	30.2	-27.8
10	2	-349	22.3	-22.2
10	2	-350	18.3	17.6
10	2	-351	20.7	20.6
10	2	-352	10.9	-10.4
10	2	-353	22.1	19.7
10	2	-354	11.8	11.9
10	2	-355	8.3	8.7
10	2	-356	35.9	-33.5
10	2	-357	19.7	18.3
10	2	-358	6.6	6.1
10	2	-359	29.3	-29.2
10	2	-360	21.4	-17.3
10	2	-361	29.0	29.8
10	2	-362	23.1	21.8
10	2	-363	30.2	-27.8
10	2	-364	22.3	-22.2
10	2	-365	18.3	17.6
10	2	-366	20.7	20.6
10	2	-367	10.9	-10.4
10	2	-368	22.1	19.7
10	2	-369	11.8	11.9
10	2	-370	8.3	8.7
10	2	-371	35.9	-33.5
10	2	-372	19.7	18.3
10	2	-373	6.6	6.1
10	2	-374	29.3	-29.2
10	2	-375	21.4	-17.3
10	2	-376	29.0	29.8
10	2	-377	23.1	21.8
10	2	-378	30.2	-27.8
10	2	-379	22.3	-22.2
10	2	-380	18.3	17.6
10	2	-381	20.7	20.

H	K	L	F OBS	F CALC
4	5	11	7.9	-11.9
4	5	12	11.7	12.4
4	5	13	25.2	-24.1
4	5	14	16.6	-13.9
4	5	15	47.9	49.2
4	5	16	13.5	-11.7
4	5	17	35.3	33.3
4	5	18	69.5	68.2
4	5	19	75.0	77.9
4	6	0	50.1	51.1
4	6	1	15.2	15.2
4	6	2	21.2	22.3
4	6	3	13.4	-13.5
4	6	4	46.8	-46.6
4	6	5	43.3	41.6
4	6	6	35.0	34.8
4	6	7	67.4	-68.4
4	6	8	69.6	69.2
4	6	9	75.0	77.7
4	6	10	50.1	51.1
4	6	11	15.2	15.2
4	6	12	21.2	22.3
4	6	13	13.4	-13.5
4	6	14	46.8	-46.6
4	6	15	43.3	41.6
4	6	16	35.0	34.8
4	6	17	67.4	-68.4
4	6	18	69.6	69.2
4	6	19	75.0	77.7
4	7	0	50.1	51.1
4	7	1	15.2	15.2
4	7	2	21.2	22.3
4	7	3	13.4	-13.5
4	7	4	46.8	-46.6
4	7	5	43.3	41.6
4	7	6	35.0	34.8
4	7	7	67.4	-68.4
4	7	8	69.6	69.2
4	7	9	75.0	77.7
4	7	10	50.1	51.1
4	7	11	15.2	15.2
4	7	12	21.2	22.3
4	7	13	13.4	-13.5
4	7	14	46.8	-46.6
4	7	15	43.3	41.6
4	7	16	35.0	34.8
4	7	17	67.4	-68.4
4	7	18	69.6	69.2
4	7	19	75.0	77.7
4	8	0	50.1	51.1
4	8	1	15.2	15.2
4	8	2	21.2	22.3
4	8	3	13.4	-13.5
4	8	4	46.8	-46.6
4	8	5	43.3	41.6
4	8	6	35.0	34.8
4	8	7	67.4	-68.4
4	8	8	69.6	69.2
4	8	9	75.0	77.7
4	8	10	50.1	51.1
4	8	11	15.2	15.2
4	8	12	21.2	22.3
4	8	13	13.4	-13.5
4	8	14	46.8	-46.6
4	8	15	43.3	41.6
4	8	16	35.0	34.8
4	8	17	67.4	-68.4
4	8	18	69.6	69.2
4	8	19	75.0	77.7
4	9	0	50.1	51.1
4	9	1	15.2	15.2
4	9	2	21.2	22.3
4	9	3	13.4	-13.5
4	9	4	46.8	-46.6
4	9	5	43.3	41.6
4	9	6	35.0	34.8
4	9	7	67.4	-68.4
4	9	8	69.6	69.2
4	9	9	75.0	77.7
4	9	10	50.1	51.1
4	9	11	15.2	15.2
4	9	12	21.2	22.3
4	9	13	13.4	-13.5
4	9	14	46.8	-46.6
4	9	15	43.3	41.6
4	9	16	35.0	34.8
4	9	17	67.4	-68.4
4	9	18	69.6	69.2
4	9	19	75.0	77.7
4	10	0	50.1	51.1
4	10	1	15.2	15.2
4	10	2	21.2	22.3
4	10	3	13.4	-13.5
4	10	4	46.8	-46.6
4	10	5	43.3	41.6
4	10	6	35.0	34.8
4	10	7	67.4	-68.4
4	10	8	69.6	69.2
4	10	9	75.0	77.7
4	10	10	50.1	51.1
4	10	11	15.2	15.2
4	10	12	21.2	22.3
4	10	13	13.4	-13.5
4	10	14	46.8	-46.6
4	10	15	43.3	41.6
4	10	16	35.0	34.8
4	10	17	67.4	-68.4
4	10	18	69.6	69.2
4	10	19	75.0	77.7
4	11	0	50.1	51.1
4	11	1	15.2	15.2
4	11	2	21.2	22.3
4	11	3	13.4	-13.5
4	11	4	46.8	-46.6
4	11	5	43.3	41.6
4	11	6	35.0	34.8
4	11	7	67.4	-68.4
4	11	8	69.6	69.2
4	11	9	75.0	77.7
4	11	10	50.1	51.1
4	11	11	15.2	15.2
4	11	12	21.2	22.3
4	11	13	13.4	-13.5
4	11	14	46.8	-46.6
4	11	15	43.3	41.6
4	11	16	35.0	34.8
4	11	17	67.4	-68.4
4	11	18	69.6	69.2
4	11	19	75.0	77.7
4	12	0	50.1	51.1
4	12	1	15.2	15.2
4	12	2	21.2	22.3
4	12	3	13.4	-13.5
4	12	4	46.8	-46.6
4	12	5	43.3	41.6
4	12	6	35.0	34.8
4	12	7	67.4	-68.4
4	12	8	69.6	69.2
4	12	9	75.0	77.7
4	12	10	50.1	51.1
4	12	11	15.2	15.2
4	12	12	21.2	22.3
4	12	13	13.4	-13.5
4	12	14	46.8	-46.6
4	12	15	43.3	41.6
4	12	16	35.0	34.8
4	12	17	67.4	-68.4
4	12	18	69.6	69.2
4	12	19	75.0	77.7
4	13	0	50.1	51.1
4	13	1	15.2	15.2
4	13	2	21.2	22.3
4	13	3	13.4	-13.5
4	13	4	46.8	-46.6
4	13	5	43.3	41.6
4	13	6	35.0	34.8
4	13	7	67.4	-68.4
4	13	8	69.6	69.2
4	13	9	75.0	77.7
4	13	10	50.1	51.1
4	13	11	15.2	15.2
4	13	12	21.2	22.3
4	13	13	13.4	-13.5
4	13	14	46.8	-46.6
4	13	15	43.3	41.6
4	13	16	35.0	34.8
4	13	17	67.4	-68.4
4	13	18	69.6	69.2
4	13	19	75.0	77.7
4	14	0	50.1	51.1
4	14	1	15.2	15.2
4	14	2	21.2	22.3
4	14	3	13.4	-13.5
4	14	4	46.8	-46.6
4	14	5	43.3	41.6
4	14	6	35.0	34.8
4	14	7	67.4	-68.4
4	14	8	69.6	69.2
4	14	9	75.0	77.7
4	14	10	50.1	51.1
4	14	11	15.2	15.2
4	14	12	21.2	22.3
4	14	13	13.4	-13.5
4	14	14	46.8	-46.6
4	14	15	43.3	41.6
4	14	16	35.0	34.8
4	14	17	67.4	-68.4
4	14	18	69.6	69.2
4	14	19	75.0	77.7
4	15	0	50.1	51.1
4	15	1	15.2	15.2
4	15	2	21.2	22.3
4	15	3	13.4	-13.5
4	15	4	46.8	-46.6
4	15	5	43.3	41.6
4	15	6	35.0	34.8
4	15	7	67.4	-68.4
4	15	8	69.6	69.2
4	15	9	75.0	77.7
4	15	10	50.1	51.1
4	15	11	15.2	15.2
4	15	12	21.2	22.3
4	15	13	13.4	-13.5
4	15	14	46.8	-46.6
4	15	15	43.3	41.6
4	15	16	35.0	34.8
4	15	17	67.4	-68.4
4	15	18	69.6	69.2
4	15	19	75.0	77.7
4	16	0	50.1	51.1
4	16	1	15.2	15.2
4	16	2	21.2	22.3
4	16	3	13.4	-13.5
4	16	4	46.8	-46.6
4	16	5	43.3	41.6
4	16	6	35.0	34.8
4	16	7	67.4	-68.4
4	16	8	69.6	69.2
4	16	9	75.0	77.7
4	16	10	50.1	51.1
4	16	11	15.2	15.2
4	16	12	21.2	22.3
4	16	13	13.4	-13.5
4	16	14	46.8	-46.6
4	16	15	43.3	41.6
4	16	16	35.0	34.8
4	16	17	67.4	-68.4
4	16	18	69.6	69.2
4	16	19	75.0	77.7
4	17	0	50.1	51.1
4	17	1	15.2	15.2
4	17	2	21.2	22.3
4	17	3	13.4	-13.5
4	17	4	46.8	-46.6
4	17	5	43.3	41.6
4	17	6	35.0	34.8
4	17	7	67.4	-68.4
4	17	8	69.6	69.2
4	17	9	75.0	77.7
4	17	10	50.1	51.1
4	17	11	15.2	15.2
4	17	12	21.2	22.3
4	17	13	13.4	-13.5
4	17	14	46.8	-46.6
4	17	15	43.3	41.6
4	17	16	35.0	34.8
4	17	17	67.4	-68.4
4	17	18	69.6	69.2
4	17	19	75.0	77.7
4	18	0	50.1	51.1
4	18	1	15.2	15.2
4	18	2	21.2	22.3
4	18	3	13.4	-13.5
4	18	4	46.8	-46.6
4	18	5	43.3	41.6
4	18	6	35.0	34.8
4	18	7	67.4	-68.4
4	18	8	69.6	69.2
4	18	9	75.0	77.7
4	18	10	50.1	51.1
4	18	11	15.2	15.2
4	18	12	21.2	22.3
4	18	13	13.4	-13.5
4	18	14	46.8	-46.6
4	18	15	43.3	41.6
4	18	16	35.0	34.8
4	18	17	67.4	-68.4
4	18	18	69.6	69.2
4	18	19	75.0	77.7
4	19	0	50.1	51.1
4	19	1	15.2	15.2
4	19	2	21.2	22.3
4	19	3	13.4	-13.5
4	19	4	46.8	-46.6
4	19	5	43.3	41.6
4	19	6	35.0	34.8
4	19	7	67.4	-68.4
4	19	8	69.6	69.2
4	19	9	75.0	77.7
4	19	10	50.1	51.1
4	19	11	15.2	15.2
4	19	12	21.2	22.3
4	19	13	13.4	-13.5
4	19	14	46.8	-46.6
4	19	15	43.3	41.6
4	19	16	35.0	34.8
4	19	17	67.4	-68.4
4	19	18	69.6	69.2
4	19	19	75.0	77.7
4	20	0	50.1	51.1
4	20	1	15.2	15.2
4	20	2	21.2	22.3
4	20	3	13.4	-13.5
4	20	4	46.8	-46.6
4	20	5	43.3	41.6
4	20	6	35.0	34.8
4	20	7	67.4	-68.4
4	20	8	69.6	69.2
4	20	9	75.0	77.7
4	20	10	50.1	51.1
4	20	11	15.2	15.2
4	20	12	21.2	22.3
4	20	13	13.4	-13.5
4	20	14	46.8	-46.6
4	20	15	43.3	41.6
4	20	16	35.0	34.8
4	20	17	67.4	-68.4
4	20	18	69.6	69.2
4	20	19	75.0	77.7
4	21	0	50.1	51.1
4	21	1	15.2	15.2
4	21	2	21.2	22.3
4	21	3	13.4	-13.5
4	21	4	46.8	-46.6
4	21	5	43.3	41.6
4	21	6	35.0	34.8
4	21	7	67.4	-68.4
4	21	8	69.6	69.2
4	21	9	75.0	77.7
4	21	10	50.1	51.1
4	21	11	15.2	15.2
4	21	12	21.2	22.3
4	21	13	13.4	-13.5
4	21	14	46.8	-46.6
4	21	15	43.3	41.6
4	21	16	35.0	34.8
4	21	17	67.4	-68.4
4	21	18	69.6	69.2
4	21	19	75.0	77.7
4	22	0	50.1	51.1
4	22	1	15.2	15.2
4	22	2	21.2	22.3
4	22	3	13.4	-13.5
4	22	4	46.8	-46.6
4	22	5	43.3	41.6
4	22	6	35.0	34.8
4	22	7	67.4	-68.4
4	22	8	69.6	69.2
4	22	9	75.0	77.7
4	22	10	50.1	51.1
4	22	11	15.2	15.2
4	22	12	21.2	22.3
4	22	13	13.4	-13.5
4	22	14	46.8	-46.6
4	22	15	43.3	41.6
4	22	16	35.0	34.8
4	22	17	67.4	-68.4
4	22	18	69.6	69.2
4	22	19	75.0	77.7
4	23	0	50.1	51.1
4	23	1	15.2	15.2
4	23	2	21.2	22.3
4	23	3	13.4	-13.5
4	23	4	46.8	-46.6
4	23	5	43.3	41.6
4	23	6	35.0	34.8
4	23	7	67.4	-68.4
4	23	8	69.6	69.2
4	23	9	75.0	77.7
4	23	10	50.1	51.1
4	23	11	15.2	15.2
4	23	12	21.2	22.3
4	23	13	13.4	-13.5
4	23	14	46.8	-46.6
4	23	15	43.3	41.6
4	23	16	35.0	34.8
4	23	17	67.4	-68.4
4	23	18	69.6	69.2
4	23	19	75.0	77.7
4	24	0	50.1	51.1
4	24	1	15.2	15.2
4	24	2	21.2	22.3
4	24	3	13.4	-13.5
4	24	4	46.8	-46.6
4	24	5	43.3	41.6
4	24	6	35.0	34.8
4	24	7	67.4	-68.4
4	24	8	69.6	69.2
4	24	9	75.0	77.7
4	24	10	50.1	51.1
4	24	11	15.2	15.2
4	24	12	21.2	22.3
4	24	13	13.4	-13.5
4	24	14	46.8	-46.6
4	24	15	43.3	41.6
4	24	16	35.0	34.8
4	24	17	67.4	-68.4
4	24	18	69.6	69.2
4	24	19	75.0	77.7
4	25	0	50.1	51.1
4	25	1	15.2	15.2
4	25	2	21.2	22.3
4	25	3	13.4	-13.5
4	25	4	46.8	-46.6
4	25	5	43.3	41.6
4	25	6	35.0	34.8
4	25	7	67.4	-68.4
4	25	8	69.6	69.2
4	25	9	75.0	77.7
4	25	10	50.1	51.1
4	25	11	15.2	15.2
4	25	12	21.2	22.3
4	25	13	13.4	-13.5
4	25	14	46.8	-46.6
4	25	15	43.3	41.6
4	25	16	35.0	34.8
4	25	17	67.4	-68.4
4	25	18	69.6	69.2
4	25	19	75.0	77.7
4	26	0	50.1	51.1
4	26	1	15.2	15.2
4	26	2	21.2	22.3
4	26	3	13.4	-13.5
4	26	4	46.8	-46.6
4	26	5	43.3	41.6
4	26	6	35.0	34.8
4	26	7	67.4	-68.4
4	26	8	69.6	69.2
4	26	9	75.0	77.7
4	26	10	50.1	51.1
4	26	11	15.2	15.2
4	26	12	21.2	22.3
4	26	13	13.4	-13.5
4	26	14	46.8	-46.6
4	26	15	43.3	41.6
4	26	16	35.0	34.8
4	26	17	67.4	-68.4
4	26	18	69.6	69.2
4	26	19	75.0	77.7
4	27	0	50.1	51.1
4	27	1	15.2	15.2
4	27	2	21.2	22.3
4	27	3	13.4	-13.5
4	27	4	46.8	-46.6
4	27	5	43.3	41.6
4	27	6	35.0	34.8
4	27	7	67.4	-68.4
4	27	8	69.6	69.2
4	27	9	75.0	77.7
4	27	10	50.1	51.1
4	27	11	15.2	15.2
4	27	12	21.2	22.3
4	27	13	13.4	-13.5
4	27	14	46.8	-46.6
4	27	15	43.3	41.6
4	27	16	35.0	34.8
4	27	17	67.4	-68.4
4	27	18	69.6	69.2
4	27	19	75.0	77.7
4	28	0	50.1	51.1
4	28	1	15.2	15.2
4	28	2	21.2	22.3
4	28	3	13.4	-13.5
4	28	4	46.8	-46.6
4	28	5	43.3	41.6
4	28	6	35.0	34.8
4	28	7	67.4	-68.4
4	28	8	69.6	69.2
4	28	9	75.0	77.7
4	28	10	50.1	51.1
4	28	11	15.2	15.2
4	28	12	21.2	22.3
4	28	13	13.4	-13.5
4	28	14	46.8	-46.6
4	28	15	43.3	41.6
4	28	16	35.0	34.8
4	28	17	67.4	-68.4
4	28	18	69.6	69.2
4	28	19	75.0	77.7
4	29	0	50.1	51.1
4	29	1	15.2	15.2
4	29	2	21.2	22.3
4	29	3	13.4	-13.5
4	29	4	46.8	-46.6
4	29	5	43.3	41.6
4	29	6	35.0	34.8
4	29	7	67.4	-68.4
4	29	8	69.6	69.2
4	29	9	75.0	77.7
4	29	10	50.1	51.1
4	29	11	15.2	15.2
4	29	12	21.2	22.3
4	29	13	13.4	-13.5
4	29	14	46.8	-46.6
4	29	15	43.3	41.6
4	29	16	35.0	34.8
4	29	17	67.4	-68.4
4	29	18	69.6	69.2
4	29	19	75.0	77.7
4	30	0	50.1	51.1
4	30	1	15.2	15.2
4	30	2	21.2	22.3
4	30	3	13.4	-13.5
4	30	4	46.8	-46.6
4	30	5	43.3	41.6
4	30	6	35.0	34.8
4	30	7	67.4	-68.4
4	30	8	69.6	69.2
4	30	9	75.0	77.7
4	30	10	50.1	51.1
4	30	11	15.2	15.2
4	30	12	21.2	22.3
4	30	13	13.4	-13.5
4	30	14	46.8	-46.6
4	30	15	43.3	41.6
4	30	16	35.0	34.8
4	30	17	67.4	-68.4
4	30	18	69.6	69.2
4	30	19	75.0	77.7
4	31	0	50.1	51.1
4	31	1	15.2	15.2
4	31	2	21.2	22.3
4	31	3	13.4	-13.5
4	31	4	46.8	-46.6
4	31	5	43.3	41.6
4	31	6	35.0	34.8
4	31	7	67.4	-68.4
4	31	8	69.6	69.2
4	31	9	75.0	77.7
4	31	10	50.1	51.1
4	31	11	15.2	15.2
4	31	12	21.2	22.3
4	31	13	13.4	-13.5
4	31	14	46.8	-46.6
4	31	15	43.3	41.6
4	31	16	35.0	34.8
4	31	17	67.4	-68.4
4	31	18	69.6	69.2
4	31	19	75.0	77.7
4	32	0	50.1	51.1
4	32	1	15.2	15.2
4	32	2	21.2	22.3
4	32	3	13.4	-13.5
4	32	4	46.8	-46.6
4	32	5	43.3	41.6
4	32	6	35.0	34.8
4	32	7	67.4	-68.4
4	32	8	69.6	69.2
4	32	9	75.0	77.7
4	32	10	50.1	51.1
4	32	11	15.2	15.2
4	32	12	21.2	22.3
4	32	13	13.4	-13.5
4	32	14	46.8	-46.6
4	32	15	43.3	41.6
4	32	16	35.0	34.8
4	32	17	67.4	-68.4
4	32	18	69.6	69.2
4	32	19	75.0	77.7
4	33	0	50.1	51.1
4	33	1	15.2	15.2
4	33	2	21.2	22.3
4	33	3	13.4	-13.5
4	33	4	46.8	-46.6
4	33	5	43.3	41.6
4	33	6	35.0	34.8
4	33	7	67.4	-68.4
4	33	8	69.6	69.2
4	33	9	75.0	77.7
4	33	10	50.1	51.1
4	33	11	15.2	15.2
4	33	12	21.2	22.3
4	33	13	13.4	-13.5
4	33	14	46.8	-46.6
4	33	15	43.3	41.6
4	33	16	35.0	34.8
4	33	17	67.4	-68.4
4	33	18	69.6	69.2
4	33	19	75.0	77.7
4	34	0	50.1	51.1
4	34	1	15.2	15.2
4	34	2	21.2	22.3
4	34	3	13.4	-13.5
4	34	4	46.8	-46.6
4	34	5	43.3	41.6
4	34	6	35.0	34.8
4	34	7	67.4	-68.4
4	34	8	69.6	69.2
4	34	9	75.0	77.7
4	34	10	50.1	51.1
4	34	11	15.2	15.2
4	34	12	21.2	22.3
4	34	13	13.4	-13.5
4	34	14	46.8	-46.6
4	34	15	43.3	41.6
4	34	16	35.0	34.8
4	34	17	67.4	-68.4
4	34	18	69.6	69.2
4	34	19	75.0	77.7
4	35	0	50.1	51.1
4	35	1	15.2	15.2
4	35	2	21.2	22.3
4	35	3	13.4	-13.5
4	35	4	46.8	-46.6
4	35	5	43.3	41.6
4	35	6	35.0	34.8
4	35	7	67.4	-68.4
4	35	8	69.6	69.2
4	35	9	75.0	77.7
4	35	10	50.1	51.1
4	35	11	15.2	15.2
4	35	12	21.2	22.3
4	35	13	13.4	-13.5
4	35	14	46.8	-46.6
4	35	15	43.3	41.6
4	35	16	35.0	34.8
4	35	17	67.4	-68.4
4	35	18	69.6	69.2
4	35	19	75.0	77.7
4	36	0	50.1	51.1
4	36	1	15.2	15.2
4	36	2	21.2	22.3
4	36	3	13.4	-13.5
4	36	4	46.8	-46.6
4

TABLE 17

$Zn(py)_3(NO_3)_2$

Observed and final-calculated structure amplitudes

TABLE 18

$Co(py)_3(NO_3)_2$

(a) Atom positions (fractional coordinates)

	x/a	y/b	z/c
Co	0.5	0.70225(20)	0.25
C(1)	0.3846(9)	0.5846(13)	0.3746(8)
C(2)	0.3515(10)	0.5739(17)	0.4469(9)
C(3)	0.3921(12)	0.6737(17)	0.5132(9)
C(4)	0.4678(13)	0.7764(15)	0.5065(8)
C(5)	0.4931(11)	0.7780(12)	0.4304(8)
C(6)	0.4102(9)	0.9983(12)	0.2549(8)
C(7)	0.4067(11)	0.1443(14)	0.2546(8)
C(8)	0.5	1.2210(15)	0.25
O(1)	0.3859(8)	0.5262(9)	0.1882(5)
O(2)	0.3150(7)	0.7314(9)	0.1616(6)
O(3)	0.2186(7)	0.5502(11)	0.0917(6)
N(1)	0.4513(7)	0.6889(9)	0.3642(5)
N(2)	0.3043(8)	0.5978(11)	0.1450(6)
N(3)	0.5	0.9273(12)	0.25

TABLE 18 (cont)

(b) Anisotropic temperature factors (Å^2) *

	U_{11}	U_{22}	U_{33}	$2U_{32}$	$2U_{31}$	$2U_{12}$
Co	0.047	0.039	0.045	0.000	0.040	0.000
C(1)	0.049	0.075	0.066	0.030	0.047	-0.002
C(2)	0.052	0.093	0.075	0.044	0.063	-0.028
C(3)	0.083	0.093	0.065	0.025	0.059	0.005
C(4)	0.093	0.080	0.058	-0.008	0.062	-0.009
C(5)	0.090	0.058	0.058	0.000	0.065	-0.005
C(6)	0.053	0.056	0.068	-0.017	0.036	0.030
C(7)	0.079	0.054	0.077	0.003	0.068	0.019
C(8)	0.083	0.037	0.061	0.000	0.038	0.000
O(1)	0.077	0.070	0.065	0.019	0.032	0.019
O(2)	0.078	0.053	0.092	-0.021	0.068	0.000
O(3)	0.053	0.105	0.090	-0.064	0.037	-0.029
N(1)	0.053	0.055	0.050	-0.005	0.044	-0.010
N(2)	0.048	0.076	0.057	-0.030	0.048	-0.028
N(3)	0.052	0.039	0.058	0.000	0.043	0.000

(c) Mean estimated standard deviations (Å^2)

Co	0.001	0.001	0.001	-	0.002	-
C	0.007	0.010	0.007	0.013	0.011	0.012
O	0.006	0.006	0.006	0.009	0.009	0.009
N	0.005	0.005	0.005	0.009	0.008	0.008

* These are the values of U_{ij} in equation (5) (Section I.1.4(b)).

TABLE 19

$Cu(py)_3(NO_3)_2$

(a) Atom positions (fractional coordinates)

	x/a	y/b	z/c
Cu	0.5	0.69890(12)	0.25
C(1)	0.3851(7)	0.5925(11)	0.3703(6)
C(2)	0.3856(8)	0.5804(14)	0.4460(7)
C(3)	0.4039(11)	0.6751(14)	0.5153(9)
C(4)	0.4761(12)	0.7749(14)	0.5050(8)
C(5)	0.5042(9)	0.7800(13)	0.4290(6)
C(6)	0.4067(8)	0.9951(9)	0.2496(7)
C(7)	0.4058(9)	1.1504(10)	0.2479(7)
C(8)	0.5	1.2212(15)	0.25
O(1)	0.3804(6)	0.5354(8)	0.1876(5)
O(2)	0.2862(8)	0.7280(10)	0.1458(7)
O(3)	0.2176(7)	0.5187(12)	0.0917(7)
N(1)	0.4569(6)	0.6912(7)	0.3605(5)
N(2)	0.2934(6)	0.5951(10)	0.1397(5)
N(3)	0.5	0.9232(10)	0.25

TABLE 19 (cont)

(b) Anisotropic temperature factors ($Å^2$) *

	U_{11}	U_{22}	U_{33}	$2U_{32}$	$2U_{31}$	$2U_{12}$
Cu	0.051	0.030	0.053	0.000	0.049	0.000
C(1)	0.058	0.059	0.049	-0.024	0.038	-0.043
C(2)	0.064	0.089	0.063	0.004	0.070	-0.041
C(3)	0.078	0.081	0.074	0.023	0.095	0.009
C(4)	0.094	0.061	0.061	-0.002	0.069	0.014
C(5)	0.080	0.044	0.044	-0.009	0.062	-0.015
C(6)	0.062	0.051	0.077	-0.019	0.058	0.012
C(7)	0.072	0.035	0.074	-0.018	0.049	0.009
C(8)	0.070	0.027	0.098	0.000	0.080	0.000
O(1)	0.068	0.059	0.062	-0.008	0.046	0.004
O(2)	0.083	0.046	0.101	-0.024	0.100	-0.041
O(3)	0.059	0.107	0.099	-0.085	0.028	-0.041
N(1)	0.050	0.040	0.053	0.000	0.052	0.003
N(2)	0.041	0.064	0.063	-0.024	0.040	-0.026
N(3)	0.064	0.023	0.055	0.000	0.061	0.000

(c) Mean estimated standard deviations ($Å^2$)

Cu	0.001	0.001	0.001	-	0.001	-
C	0.005	0.006	0.005	0.009	0.008	0.009
O	0.004	0.005	0.006	0.008	0.007	0.007
N	0.003	0.004	0.004	0.006	0.006	0.005

* These are the values of U_{ij} in equation (5) (Section I.1.4(b))

TABLE 20

$Zn(py)_3(NO_3)_2$

(a) Atom positions (fractional coordinates)

	x/a	y/b	z/c
Zn	0.5	0.70834(22)	0.25
C(1)	0.3845(10)	0.5829(17)	0.3747(9)
C(2)	0.3532(9)	0.5687(16)	0.4464(9)
C(3)	0.3893(12)	0.6700(18)	0.5133(11)
C(4)	0.4622(13)	0.7720(20)	0.5043(11)
C(5)	0.4339(15)	0.7821(18)	0.4321(9)
C(6)	0.4120(13)	1.0078(16)	0.2540(11)
C(7)	0.4059(11)	1.1530(15)	0.2510(9)
C(8)	0.5	1.2321(22)	0.25
O(1)	0.3779(9)	0.5364(14)	0.1885(8)
O(2)	0.3079(9)	0.7378(12)	0.1572(8)
O(3)	0.2151(8)	0.5523(15)	0.0908(8)
N(1)	0.4524(8)	0.6874(12)	0.3636(6)
N(2)	0.2958(8)	0.6086(13)	0.1421(7)
N(3)	0.5	0.9425(13)	0.25

TABLE 20 (cont)

(b) Anisotropic temperature factors ($\AA^2$) *

	U_{11}	U_{22}	U_{33}	$2U_{32}$	$2U_{31}$	$2U_{12}$
Zn(1)	0.039	0.036	0.032	0.000	0.016	0.000
C(1)	0.040	0.063	0.038	-0.011	0.043	0.016
C(2)	0.054	0.075	0.044	-0.032	0.021	0.032
C(3)	0.068	0.099	0.038	-0.022	0.042	-0.016
C(4)	0.101	0.078	0.011	0.004	0.052	0.002
C(5)	0.070	0.053	0.051	0.019	0.041	0.040
C(6)	0.046	0.052	0.044	0.001	0.039	-0.008
C(7)	0.060	0.045	0.082	0.016	0.071	-0.018
C(8)	0.035	0.066	0.023	0.000	0.002	0.000
O(1)	0.066	0.092	0.058	0.002	0.028	0.016
O(2)	0.078	0.048	0.092	-0.022	0.087	-0.015
O(3)	0.044	0.101	0.069	-0.066	-0.007	-0.048
N(1)	0.037	0.063	0.017	-0.013	0.017	-0.004
N(2)	0.029	0.054	0.040	-0.005	0.012	0.006
N(3)	0.025	0.014	0.023	0.000	-0.016	0.000

(c) Mean estimated standard deviations ($\AA^2$)

Zn	0.002	0.001	0.001	-	0.002	-
C	0.014	0.011	0.008	0.014	0.017	0.018
O	0.011	0.009	0.008	0.012	0.013	0.014
N	0.010	0.007	0.006	0.010	0.014	0.012

* These are the values of U_{ij} in equation (5) (Section I.1.4(b))

APPENDIX V

EXPERIMENTAL

DINITRATOTRIS(PYRIDINE)-CADMIUM(II)

Preparation of Crystals

The complex was prepared by standard literature methods [170] and was recrystallised from ethanol-2,2-dimethoxypropane (1:1) containing a small amount of pyridine. The crystals were enclosed in a thin-walled glass capillary to prevent decomposition.

Crystal Data

$C_{15}H_{15}N_5O_6Cd$

M = 473.8

Monoclinic

a = 12.434 ± 0.007, b = 9.494 ± 0.005, c = 17.385 ± 0.009 Å, β = 115.42 ± 0.03°, U = 1853 Å^3

D_m = 1.70, Z = 4, D_c = 1.70

F(000) = 944

Space group C2/c (C_{2h}^6, No 15) from systematic absences: hkℓ for h + k odd, h0ℓ for ℓ odd

Mo-K_α X-rays, λ = 0.7107 Å

μ(Mo-K_α) = 12.2 cm^{-1}

Crystallographic Measurements

The initial unit-cell parameters were determined from oscillation and Weissenberg photographs taken with Cu-K_α (λ = 1.5418 Å) and from precession photographs taken with Mo-K_α radiation. These were subsequently adjusted by least-squares refinement of θ, χ , and ϕ setting angles of twelve reflections determined on a Hilger and Watts Y 290 diffractometer.

For the intensity measurements zirconium-filtered molybdenum radiation was used and 2698 independent reflections were collected by use of the θ-2θ scan technique. Of these some 2082 reflections were considered observed using the criteria $I \geqslant 1\sigma(I)$, where σ was determined from counter statistics. Values of I were corrected for Lorentz-polarisation effects but no corrections for absorption were made.

Structure Determination and Refinement

The entire structure was determined by conventional Patterson and electron-density calculations with initial phasing appropriate to the cadmium. Several cycles of structure-factor and electron-density calculations effected preliminary refinement and reduced R to 0.25. During these preliminary calculations an overall vibration parameter (U_{iso} = 0.06 $Å^2$) was assigned to the atoms.

The least-squares refinement of positional, thermal and scale parameters converged after 9 cycles, when R was 0.10 and R' was 0.015. After cycle 5 a difference Fourier synthesis was calculated which revealed positions for all the hydrogen atoms. In subsequent calculations these were included with isotropic vibration parameters (U_{iso} = 0.06 $Å^2$) but were not refined. Removal of those planes for which $I \geqslant 3\sigma(I)$ left 1491 independent data and a structure-factor calculation using the final parameters resulted in R 0.08 and R' 0.010 (details of the refinement are given in Table 21).

In all refinement cycles, the weighting scheme given as equation (32) (Section I.1.8(b)) was applied to the data. Initially the p parameters were chosen to give unit weight to all reflections, but they were later varied as indicated by a $|F_o|$ and $(\sin\theta/\lambda)$ analysis of $\sum w\Delta^2$. The final values are : p_1 50, p_2 0.001, p_3 0.0001, p_4 0.

At the conclusion of the refinement a difference synthesis and final electron-density distribution were calculated. These revealed no errors in the structure.

In all the structure-factor calculations, the atomic scattering factors used are those given in ref. 212. Observed and calculated structure factors are listed in Table 22. Fractional coordinates of all non-hydrogen atoms are given in Table 23 and the anisotropic

thermal parameters in Table 24.

The relevant interatomic dimensions and some calculated least-squares best planes through the molecule are given in Section II.2.3. The estimated standard deviations recorded were derived from the inverse of the least-squares normal-equation matrix, and are probably best regarded as minimum values.

TABLE 21

Course of refinement

Cycles	Parameters refined	Final $\underline{R}$	Final $\underline{R'}$
1 - 3	$\underline{x}$, $\underline{y}$, $\underline{z}$, $\underline{U}_{iso}$ for Cd, N, 0, C; one overall scale, unit weights, full matrix	0.146	0.031
4 - 5	$\underline{x}$, $\underline{y}$, $\underline{z}$, $\underline{U}_{iso}$ for Cd, N, 0, C; H atoms included but not refined, one overall scale, weighting scheme adjusted, full matrix	0.143	0.026
6 - 9	$\underline{x}$, $\underline{y}$, $\underline{z}$, $\underline{U}_{ij}$ ($\underline{i}$, $\underline{j}$ = 1, 2, 3) for Cd, N, 0, C; H atoms included but not refined, small adjustments to weighting scheme, full matrix	0.108	0.015

TABLE 22

$Cd(py)_2(NO_3)_2$

Observed and final-calculated structure factors

H	K	L	F OBS	F CALC
15	3	1	19.0	-6.8
15	3	0	12.4	12.4
14	4	3	17.5	14.3
14	4	2	13.5	-12.1
14	4	1	15.6	16.4
14	4	0	18.3	13.5
14	3	3	15.5	9.9
14	3	2	17.0	-17.5
14	3	1	10.2	-4.3
14	3	0	20.3	14.8
14	2	4	20.8	22.5
14	2	3	20.9	-20.4
14	2	2	17.7	18.4
14	2	1	13.0	-13.9
14	2	0	10.9	-10.7
13	5	2	10.9	15.2
13	5	1	13.9	-14.3
13	4	5	15.7	15.5
13	4	4	14.6	19.5
13	4	3	21.2	20.4
13	4	2	21.2	-19.7
13	4	1	12.2	-2.4
13	4	0	28.7	24.9
13	3	5	17.8	-18.4
13	3	4	15.1	5.8
13	3	3	22.4	17.4
13	3	2	27.4	-29.5
13	3	1	23.2	-19.6
13	3	0	20.3	17.3
13	2	6	12.7	-13.2
13	2	5	19.5	20.6
13	2	4	24.1	19.9
13	2	3	25.5	-28.1
13	2	2	22.4	-20.7
13	2	1	19.4	25.8
13	2	0	18.8	18.9
13	1	6	12.7	-13.2
13	1	5	19.4	-15.1
13	1	4	14.5	14.5
13	1	3	26.6	-22.5
13	1	2	21.3	23.3
13	1	1	19.5	-16.9
13	1	0	27.7	-21.7
13	0	5	19.2	-21.7
13	0	4	15.2	14.5
13	0	3	20.7	-19.4
13	0	2	20.9	21.4
13	0	1	17.7	18.4
13	0	0	17.3	-17.4
12	6	4	15.1	3.1
12	6	3	15.4	19.8
12	6	2	15.7	-21.4
12	6	1	14.3	-14.3
12	6	0	21.2	20.4
12	5	5	17.8	-19.7
12	5	4	19.4	22.2
12	5	3	21.2	-20.4
12	5	2	22.4	-22.5
12	5	1	15.3	-13.2
12	5	0	19.2	18.2
12	4	6	12.8	-15.7
12	4	5	19.8	-16.7
12	4	4	20.9	18.6
12	4	3	20.9	-20.4
12	4	2	18.1	16.4
12	4	1	17.3	17.3
12	4	0	20.7	-19.4
12	3	6	17.9	17.7
12	3	5	17.4	-17.1
12	3	4	22.6	-22.0
12	3	3	27.1	-27.2
12	3	2	37.4	36.6
12	3	1	26.8	42.5
12	3	0	41.2	-46.8
12	2	7	21.9	-15.5
12	2	6	12.7	-13.2
12	2	5	23.2	23.6
12	2	4	24.1	19.9
12	2	3	19.5	-21.7
12	2	2	19.2	23.4
12	2	1	25.5	-28.1
12	2	0	22.4	-20.7
12	1	7	19.4	25.8
12	1	6	18.5	18.9
12	1	5	20.7	-17.4
12	1	4	17.3	18.2
12	1	3	20.7	-19.4
12	1	2	20.9	21.4
12	1	1	17.7	18.4
12	1	0	17.3	-17.4
12	0	6	18.5	-17.9
12	0	5	20.7	-21.7
12	0	4	26.3	29.5
12	0	3	43.7	-43.3
12	0	2	46.9	51.4
12	0	1	15.6	-7.5
11	8	1	17.9	17.4
11	7	5	20.7	-17.4
11	7	4	17.3	19.3
11	7	3	27.0	-27.6
11	7	2	24.7	-27.0
11	7	1	22.7	20.1
11	7	0	19.6	18.3
11	6	6	11.2	-9.4
11	6	5	11.2	-9.4
11	6	4	17.9	-17.0
11	6	3	19.4	-21.4
11	6	2	18.6	21.4
11	6	1	18.4	15.5
11	6	0	18.3	23.3
11	5	7	15.2	-18.1
11	5	6	19.2	-17.0
11	5	5	15.0	17.5
11	5	4	19.4	19.2
11	5	3	23.9	-22.7
11	5	2	12.8	15.0
11	5	1	19.4	17.5
11	5	0	19.2	17.0
11	4	8	10.3	10.3
11	4	7	21.9	25.0
11	4	6	27.0	32.2
11	4	5	49.0	49.3
11	4	4	24.4	24.4
11	4	3	46.7	44.6
11	4	2	51.7	48.6
11	4	1	29.2	23.0
11	4	0	24.6	24.5
11	3	14	24.9	20.5
11	3	12	20.4	22.6
11	3	11	15.8	10.9
11	3	10	11.9	12.6
11	3	9	12.2	9.1
10	10	0	13.1	9.1
10	9	1	19.3	3.0
10	8	5	17.3	19.3
10	8	4	17.3	17.3
10	8	3	19.7	15.2
10	8	2	22.0	20.6
10	8	1	24.7	19.7
10	8	0	24.7	25.1
10	7	6	15.1	3.1
10	7	5	15.4	19.8
10	7	4	27.1	21.7
10	7	3	27.1	21.8
10	7	2	34.7	34.4
10	7	1	24.1	21.4
10	7	0	24.5	24.2
10	6	7	24.5	24.2
10	6	6	47.4	44.4
10	6	5	16.4	14.4
10	6	4	21.5	20.9
10	6	3	15.6	17.7
10	6	2	15.7	15.5
10	6	1	16.4	14.9
10	6	0	15.6	17.6
10	5	8	16.4	14.9
10	5	7	17.6	17.6
10	5	6	21.5	22.2
10	5	5	21.5	18.9
10	5	4	22.6	22.6
10	5	3	15.8	10.9
10	5	2	12.2	9.1
10	5	1	12.9	12.6
10	4	8	12.2	12.2
10	4	7	15.2	15.2
10	4	6	15.2	15.2
10	4	5	15.2	15.2
10	4	4	15.2	15.2
10	4	3	15.2	15.2
10	4	2	15.2	15.2
10	4	1	15.2	15.2
10	4	0	15.2	15.2
10	3	9	15.2	15.2
10	3	8	15.2	15.2
10	3	7	15.2	15.2
10	3	6	15.2	15.2
10	3	5	15.2	15.2
10	3	4	15.2	15.2
10	3	3	15.2	15.2
10	3	2	15.2	15.2
10	3	1	15.2	15.2
10	3	0	15.2	15.2
10	2	8	15.2	15.2
10	2	7	15.2	15.2
10	2	6	15.2	15.2
10	2	5	15.2	15.2
10	2	4	15.2	15.2
10	2	3	15.2	15.2
10	2	2	15.2	15.2
10	2	1	15.2	15.2
10	2	0	15.2	15.2
10	1	8	15.2	15.2
10	1	7	15.2	15.2
10	1	6	15.2	15.2
10	1	5	15.2	15.2
10	1	4	15.2	15.2
10	1	3	15.2	15.2
10	1	2	15.2	15.2
10	1	1	15.2	15.2
10	1	0	15.2	15.2
10	0	7	15.2	15.2
10	0	6	15.2	15.2
10	0	5	15.2	15.2
10	0	4	15.2	15.2
10	0	3	15.2	15.2
10	0	2	15.2	15.2
10	0	1	15.2	15.2
10	0	0	15.2	15.2
9	9	5	15.2	15.2
9	9	4	15.2	15.2
9	9	3	15.2	15.2
9	9	2	15.2	15.2
9	9	1	15.2	15.2
9	9	0	15.2	15.2
9	8	6	15.2	15.2
9	8	5	15.2	15.2
9	8	4	15.2	15.2
9	8	3	15.2	15.2
9	8	2	15.2	15.2
9	8	1	15.2	15.2
9	8	0	15.2	15.2
9	7	7	15.2	15.2
9	7	6	15.2	15.2
9	7	5	15.2	15.2
9	7	4	15.2	15.2
9	7	3	15.2	15.2
9	7	2	15.2	15.2
9	7	1	15.2	15.2
9	7	0	15.2	15.2
9	6	8	15.2	15.2
9	6	7	15.2	15.2
9	6	6	15.2	15.2
9	6	5	15.2	15.2
9	6	4	15.2	15.2
9	6	3	15.2	15.2
9	6	2	15.2	15.2
9	6	1	15.2	15.2
9	6	0	15.2	15.2
9	5	9	15.2	15.2
9	5	8	15.2	15.2
9	5	7	15.2	15.2
9	5	6	15.2	15.2
9	5	5	15.2	15.2
9	5	4	15.2	15.2
9	5	3	15.2	15.2
9	5	2	15.2	15.2
9	5	1	15.2	15.2
9	5	0	15.2	15.2
9	4	10	15.2	15.2
9	4	9	15.2	15.2
9	4	8	15.2	15.2
9	4	7	15.2	15.2
9	4	6	15.2	15.2
9	4	5	15.2	15.2
9	4	4	15.2	15.2
9	4	3	15.2	15.2
9	4	2	15.2	15.2
9	4	1	15.2	15.2
9	4	0	15.2	15.2
9	3	11	15.2	15.2
9	3	10	15.2	15.2
9	3	9	15.2	15.2
9	3	8	15.2	15.2
9	3	7	15.2	15.2
9	3	6	15.2	15.2
9	3	5	15.2	15.2
9	3	4	15.2	15.2
9	3	3	15.2	15.2
9	3	2	15.2	15.2
9	3	1	15.2	15.2
9	3	0	15.2	15.2
9	2	8	15.2	15.2
9	2	7	15.2	15.2
9	2	6	15.2	15.2
9	2	5	15.2	15.2
9	2	4	15.2	15.2
9	2	3	15.2	15.2
9	2	2	15.2	15.2
9	2	1	15.2	15.2
9	2	0	15.2	15.2
9	1	8	15.2	15.2
9	1	7	15.2	15.2
9	1	6	15.2	15.2
9	1	5	15.2	15.2
9	1	4	15.2	15.2
9	1	3	15.2	15.2
9	1	2	15.2	15.2
9	1	1	15.2	15.2
9	1	0	15.2	15.2
9	0	7	15.2	15.2
9	0	6	15.2	15.2
9	0	5	15.2	15.2
9	0	4	15.2	15.2
9	0	3	15.2	15.2
9	0	2	15.2	15.2
9	0	1	15.2	15.2
9	0	0	15.2	15.2
8	8	6	15.2	15.2
8	8	5	15.2	15.2
8	8	4	15.2	15.2
8	8	3	15.2	15.2
8	8	2	15.2	15.2
8	8	1	15.2	15.2
8	8	0	15.2	15.2
8	7	7	15.2	15.2
8	7	6	15.2	15.2
8	7	5	15.2	15.2
8	7	4	15.2	15.2
8	7	3	15.2	15.2
8	7	2	15.2	15.2
8	7	1	15.2	15.2
8	7	0	15.2	15.2
8	6	8	15.2	15.2
8	6	7	15.2	15.2
8	6	6	15.2	15.2
8	6	5	15.2	15.2
8	6	4	15.2	15.2
8	6	3	15.2	15.2
8	6	2	15.2	15.2
8	6	1	15.2	15.2
8	6	0	15.2	15.2
8	5	8	15.2	15.2
8	5	7	15.2	15.2
8	5	6	15.2	15.2
8	5	5	15.2	15.2
8	5	4	15.2	15.2
8	5	3	15.2	15.2
8	5	2	15.2	15.2
8	5	1	15.2	15.2
8	5	0	15.2	15.2
8	4	8	15.2	15.2
8	4	7	15.2	15.2
8	4	6	15.2	15.2
8	4	5	15.2	15.2
8	4	4	15.2	15.2
8	4	3	15.2	15.2
8	4	2	15.2	15.2
8	4	1	15.2	15.2
8	4	0	15.2	15.2
8	3	8	15.2	15.2
8	3	7	15.2	15.2
8	3	6	15.2	15.2
8	3	5	15.2	15.2
8	3	4	15.2	15.2
8	3	3	15.2	15.2
8	3	2	15.2	15.2
8	3	1	15.2	15.2
8	3	0	15.2	15.2
8	2	8	15.2	15.2
8	2	7	15.2	15.2
8	2	6	15.2	15.2
8	2	5	15.2	15.2
8	2	4	15.2	15.2
8	2	3	15.2	15.2
8	2	2	15.2	15.2
8	2	1	15.2	15.2
8	2	0	15.2	15.2
8	1	8	15.2	15.2
8	1	7	15.2	15.2
8	1	6	15.2	15.2
8	1	5	15.2	15.2
8	1	4	15.2	15.2
8	1	3	15.2	15.2
8	1	2	15.2	15.2
8	1	1	15.2	15.2
8	1	0	15.2	15.2
8	0	7	15.2	15.2
8	0	6	15.2	15.2
8	0	5	15.2	15.2
8	0	4	15.2	15.2
8	0	3	15.2	15.2
8	0	2	15.2	15.2
8	0	1	15.2	15.2
8	0	0	15.2	15.2
7	7	6	15.2	15.2
7	7	5	15.2	15.2
7	7	4	15.2	15.2
7	7	3	15.2	15.2
7	7	2	15.2	15.2
7	7	1	15.2	15.2
7	7	0	15.2	15.2
7	6	8	15.2	15.2
7	6	7	15.2	15.2
7	6	6	15.2	15.2
7	6	5	15.2	15.2
7	6	4	15.2	15.2
7	6	3	15.2	15.2
7	6	2	15.2	15.2
7	6	1	15.2	15.2
7	6	0	15.2	15.2
7	5	10	15.2	15.2
7	5	9	15.2	15.2
7	5	8	15.2	15.2
7	5	7	15.2	15.2
7	5	6	15.2	15.2
7	5	5	15.2	15.2
7	5	4	15.2	15.2
7	5	3	15.2	15.2
7	5	2	15.2	15.2
7	5	1	15.2	15.2
7	5	0	15.2	15.2
7	4	9	15.2	15.2
7	4	8	15.2	15.2
7	4	7	15.2	15.2
7	4	6	15.2	15.2
7	4	5	15.2	15.2
7	4	4	15.2	15.2
7	4	3	15.2	15.2
7	4	2	15.2	15.2
7	4	1	15.2	15.2
7	4	0	15.2	15.2
7	3	10	15.2	15.2
7	3	9	15.2	15.2
7	3	8	15.2	15.2
7	3	7	15.2	15.2
7	3	6	15.2	15.2
7	3	5	15.2	15.2
7	3	4	15.2	15.2
7	3	3	15.2	15.2
7	3	2	15.2	15.2
7	3	1	15.2	15.2
7	3	0	15.2	15.2
7	2	8	15.2	15.2
7	2	7	15.2	15.2
7	2	6	15.2	15.2
7	2	5	15.2	15.2
7	2	4	15.2	15.2
7	2	3	15.2	15.2
7	2	2	15.2	15.2
7	2	1	15.2	15.2
7	2	0	15.2	15.2
7	1	8	15.2	15.2
7	1	7	15.2	15.2
7	1	6	15.2	15.2
7	1	5	15.2	15.2
7	1	4	15.2	15.2
7	1	3	15.2	15.2
7	1	2	15.2	15.2
7	1	1	15.2	15.2
7	1	0	15.2	15.2
7	0	7	15.2	15.2
7	0	6	15.2	15.2
7	0	5	15.2	15.2
7	0	4	15.2	15.2
7	0	3	15.2	15.2
7	0	2	15.2	15.2
7	0	1	15.2	15.2
7	0	0	15.2	15.2
6	6	6	15.2	15.2
6	6	5	15.2	15.2
6	6	4	15.2	15.2
6	6	3	15.2	15.2
6	6	2	15.2	15.2
6	6	1	15.2	15.2
6	6	0	15.2	15.2
6	5	8	15.2	15.2
6	5	7	15.2	15.2
6	5	6	15.2	15.2
6	5	5	15.2	15.2
6	5	4	15.2	15.2
6	5	3	15.2	15.2
6	5	2	15.2	15.2
6	5	1	15.2	15.2
6	5	0	15.2	15.2
6	4	8	15.2	15.2
6	4	7	15.2	15.2
6	4	6	15.2	15.2
6	4	5	15.2	15.2
6	4	4	15.2	15.2
6	4	3	15.2	15.2
6	4	2	15.2	15.2
6	4	1	15.2	15.2
6	4	0	15.2	15.2
6	3	8	15.2	15.2
6	3	7	15.2	15.2
6	3	6	15.2	15.2
6	3	5	15.2	15.2
6	3	4	15.2	15.2
6	3	3	15.2	15.2
6	3	2	15.2	15.2
6	3	1	15.2	15.2
6	3	0	15.2	15.2
6	2	8	15.2	15.2
6	2	7	15.2	15.2
6	2	6	15.2	15.2
6	2	5	15.2	15.2
6	2	4	15.2	15.2
6	2	3	15.2	15.2
6	2	2	15.2	15.2
6	2	1	15.2	15.2
6	2	0	15.2	15.2
6	1	8	15.2	15.2
6	1	7	15.2	15.2
6	1	6	15.2	15.2
6	1	5	15.2	15.2
6	1	4	15.2	15.2
6	1	3	15.2	15.2
6	1	2	15.2	15.2
6	1	1	15.2	15.2
6	1	0	15.2	15.2
6	0	7	15.2	15.2
6	0	6	15.2	15.2
6	0	5	15.2	15.2
6	0	4	15.2	15.2
6	0	3	15.2	15.2
6	0	2	15.2	15.2
6	0	1	15.2	15.2
6	0	0	15.2	15.2
5	5	5	15.2	15.2
5	5	4	15.2	15.2
5	5	3	15.2	15.2
5	5	2	15.2	15.2
5	5	1	15.2	15.2
5	5	0	15.2	15.2
5	4	8	15.2	15.2
5	4	7	15.2	15.2
5	4	6	15.2	15.2
5	4	5	15.2	15.2
5	4	4	15.2	15.2
5	4	3	15.2	15.2
5	4	2	15.2	15.2
5	4	1	15.2	15.2
5	4	0	15.2	15.2
5	3	8	15.2	15.2
5	3	7	15.2	15.2
5	3	6	15.2	15.2
5	3	5	15.2	15.2
5	3	4	15.2	15.2
5	3	3	15.2	15.2
5	3	2	15.2	15.2
5	3	1	15.2	15.2
5	3	0	15.2	15.2
5	2	8	15.2	15.2
5	2	7	15.2	15.2
5	2	6	15.2	15.2
5	2	5	15.2	15.2
5	2	4	15.2	15.2
5	2	3	15.2	15.2
5	2	2	15.2	15.2
5	2	1	15.2	15.2
5	2	0	15.2	15.2
5	1	8	15.2	15.2
5	1	7	15.2	15.2
5	1	6	15.2	15.2
5	1	5	15.2	15.2
5	1	4	15.2	15.2
5	1	3	15.2	15.2
5	1	2	15.2	15.2
5	1	1	15.2	15.2
5	1	0	15.2	15.2
5	0	7	15.2	15.2
5	0	6	15.2	15.2
5	0	5	15.2	15.2
5	0	4	15.2	15.2
5	0	3	15.2	15.2
5	0	2	15.2	15.2
5	0	1	15.2	15.2
5	0	0	15.2	15.2
4	4	6	15.2	15.2
4	4	5	15.2	15.2
4	4	4	15.2	15.2
4	4	3	15.2	15.2
4	4	2	15.2	15.2
4	4	1	15.2	15.2
4	4	0	15.2	15.2
4	3	8	15.2	15.2
4	3	7	15.2	15.2
4	3	6	15.2	15.2
4	3	5	15.2	15.2
4	3	4	15.2	15.2
4	3	3	15.2	15.2
4	3	2	15.2	15.2
4	3	1	15.2	15.2
4	3	0	15.2	15.2
4	2	8	15.2	15.2
4	2	7	15.2	15.2
4	2	6	15.2	15.2
4	2	5	15.2	15.2
4	2	4	15.2	15.2
4	2	3	15.2	15.2
4	2	2	15.2	15.2
4	2	1	15.2	15.2
4	2	0	15.2	15.2
4	1	8	15.2	15.2
4	1	7	15.2	15.2
4	1	6	15.2	15.2
4	1	5	15.2	15.2
4	1	4	15.2	15.2
4	1	3	15.2	15.2
4	1	2	15.2	15.2
4	1	1	15.2	15.2
4	1	0	15.2	15.2
4	0	7	15.2	15.2
4	0	6	15.2	15.2
4	0	5	15.2	15.2
4	0	4	15.2	15.2
4	0	3	15.2	15.2
4	0	2	15.2	15.2
4	0	1	15.2	15.2
4	0	0	15.2	15.2
3	3	5	15.2	15.2
3	3	4	15.2	15.2
3	3	3	15.2	15.2
3	3	2	15.2	15.2
3	3	1	15.2	15.2
3	3	0	15.2	15.2
3	2	8	15.2	15.2
3	2	7	15.2	15.2
3	2	6	15.2	15.2
3	2	5	15.2	15.2
3	2	4	15.2	15.2
3	2	3	15.2	15.2
3	2	2	15.2	15.2
3	2	1	15.2

H	K	L	F OBS	F CALC
0	0	2	39.1	39.1
0	0	4	35.2	34.0
0	0	6	44.4	47.3
0	0	8	18.3	20.5
0	0	10	66.2	68.7
0	0	12	21.6	21.4
0	0	14	76.8	71.5
0	0	16	27.3	26.5
0	0	18	19.4	19.6
0	0	20	12.8	12.9
0	1	1	9.7	9.7
0	1	3	99.2	98.6
0	1	5	122.4	123.1
0	1	7	49.2	50.9
0	1	9	21.4	17.2
0	1	11	12.3	11.5
0	1	13	24.1	24.2
0	1	15	27.1	28.5
0	1	17	24.3	25.7
0	1	19	35.0	36.1
0	1	21	32.5	35.1
0	2	2	51.0	53.0
0	2	4	54.4	51.8
0	2	6	52.6	50.2
0	2	8	98.7	92.9
0	2	10	47.3	47.3
0	2	12	117.1	106.6
0	2	14	62.3	64.1
0	2	16	64.3	64.3
0	2	18	14.8	23.2
0	2	20	17.8	16.0
0	3	1	28.0	26.3
0	3	3	22.0	29.3
0	3	5	57.2	67.6
0	3	7	29.1	31.9
0	3	9	81.0	90.6
0	3	11	55.6	59.1
0	3	13	131.4	137.0
0	3	15	87.0	89.6
0	3	17	73.9	72.3
0	3	19	17.2	17.2
0	3	21	14.3	13.8
0	4	2	97.8	93.3
0	4	4	231.4	221.6
0	4	6	175.8	183.3
0	4	8	34.9	33.0
0	4	10	60.2	66.9
0	4	12	49.0	51.7
0	4	14	147.3	135.8
0	4	16	31.9	31.6
0	4	18	74.6	66.4
0	4	20	19.5	19.4
0	5	1	15.6	11.8
0	5	3	22.4	21.7
0	5	5	22.0	24.1
0	5	7	20.9	17.2
0	5	9	13.3	12.4
0	5	11	13.0	15.5
0	5	13	17.8	20.5
0	5	15	17.0	19.8
0	5	17	28.1	24.1
0	5	19	16.0	17.7
0	5	21	25.6	25.9
0	6	2	20.4	19.3
0	6	4	31.4	33.1
0	6	6	94.8	96.0
0	6	8	28.8	30.1
0	6	10	23.5	17.1
0	6	12	20.6	19.9
0	6	14	35.5	29.8
0	6	16	23.4	28.1
0	6	18	19.4	10.9
0	6	20	19.9	17.6
0	7	1	9.9	9.9
0	7	3	48.4	48.3
0	7	5	61.8	61.0
0	7	7	19.0	16.5
0	7	9	58.4	58.4
0	7	11	20.4	20.3
0	7	13	10.9	3.0
0	7	15	23.5	17.1
0	7	17	19.9	17.6
0	7	19	23.5	17.1
0	8	2	20.4	24.9
0	8	4	11.0	3.7
0	8	6	19.9	23.6
0	8	8	34.8	30.8
0	8	10	9.7	4.6
0	8	12	15.8	10.2
0	8	14	33.5	35.8
0	8	16	10.8	14.4
0	8	18	44.1	42.0
0	8	20	14.2	12.1
0	9	1	55.6	59.1
0	9	3	131.4	137.0
0	9	5	87.0	89.6
0	9	7	73.9	72.3
0	9	9	17.2	17.2
0	9	11	14.3	13.8
0	9	13	97.8	93.3
0	9	15	231.4	221.6
0	9	17	175.8	183.3
0	9	19	34.9	33.0
0	9	21	60.2	66.9
0	10	2	49.0	51.7
0	10	4	147.3	135.8
0	10	6	31.9	31.6
0	10	8	74.6	66.4
0	10	10	19.5	19.4
0	10	12	15.6	11.8
0	10	14	22.4	21.7
0	10	16	22.0	24.1
0	10	18	20.9	17.2
0	10	20	13.3	12.4
0	11	1	13.0	15.5
0	11	3	17.8	20.5
0	11	5	17.0	19.8
0	11	7	28.1	24.1
0	11	9	16.0	17.7
0	11	11	25.6	25.9
0	11	13	20.4	19.3
0	11	15	31.4	33.1
0	11	17	94.8	96.0
0	11	19	28.8	30.1
0	11	21	23.5	17.1
0	12	2	19.9	17.6
0	12	4	23.5	17.1
0	12	6	20.4	24.9
0	12	8	11.0	3.7
0	12	10	19.9	23.6
0	12	12	34.8	30.8
0	12	14	9.7	4.6
0	12	16	15.8	10.2
0	12	18	33.5	35.8
0	12	20	10.8	14.4
0	13	1	44.1	42.0
0	13	3	14.2	12.1
0	13	5	50.2	49.0
0	13	7	31.4	29.5
0	13	9	61.2	61.2
0	13	11	23.3	23.5
0	13	13	34.8	30.8
0	13	15	9.7	4.6
0	13	17	15.8	10.2
0	13	19	33.5	35.8
0	13	21	10.8	14.4
0	14	2	44.1	42.0
0	14	4	14.2	12.1
0	14	6	50.2	49.0
0	14	8	31.4	29.5
0	14	10	61.2	61.2
0	14	12	23.3	23.5
0	14	14	34.8	30.8
0	14	16	9.7	4.6
0	14	18	15.8	10.2
0	14	20	33.5	35.8
0	15	1	10.8	14.4
0	15	3	44.1	42.0
0	15	5	14.2	12.1
0	15	7	50.2	49.0
0	15	9	31.4	29.5
0	15	11	61.2	61.2
0	15	13	23.3	23.5
0	15	15	34.8	30.8
0	15	17	9.7	4.6
0	15	19	15.8	10.2
0	15	21	33.5	35.8
0	16	2	10.8	14.4
0	16	4	44.1	42.0
0	16	6	14.2	12.1
0	16	8	50.2	49.0
0	16	10	31.4	29.5
0	16	12	61.2	61.2
0	16	14	23.3	23.5
0	16	16	34.8	30.8
0	16	18	9.7	4.6
0	16	20	15.8	10.2
0	17	1	33.5	35.8
0	17	3	10.8	14.4
0	17	5	44.1	42.0
0	17	7	14.2	12.1
0	17	9	50.2	49.0
0	17	11	31.4	29.5
0	17	13	61.2	61.2
0	17	15	23.3	23.5
0	17	17	34.8	30.8
0	17	19	9.7	4.6
0	17	21	15.8	10.2
0	18	2	33.5	35.8
0	18	4	10.8	14.4
0	18	6	44.1	42.0
0	18	8	14.2	12.1
0	18	10	50.2	49.0
0	18	12	31.4	29.5
0	18	14	61.2	61.2
0	18	16	23.3	23.5
0	18	18	34.8	30.8
0	18	20	9.7	4.6
0	19	1	15.8	10.2
0	19	3	33.5	35.8
0	19	5	10.8	14.4
0	19	7	44.1	42.0
0	19	9	14.2	12.1
0	19	11	50.2	49.0
0	19	13	31.4	29.5
0	19	15	61.2	61.2
0	19	17	23.3	23.5
0	19	19	34.8	30.8
0	19	21	9.7	4.6
0	20	2	15.8	10.2
0	20	4	33.5	35.8
0	20	6	10.8	14.4
0	20	8	44.1	42.0
0	20	10	14.2	12.1
0	20	12	50.2	49.0
0	20	14	31.4	29.5
0	20	16	61.2	61.2
0	20	18	23.3	23.5
0	20	20	34.8	30.8
1	1	0	9.7	15.0
1	1	2	99.2	98.6
1	1	4	122.4	123.1
1	1	6	49.2	50.9
1	1	8	21.4	17.2
1	1	10	12.3	11.5
1	1	12	24.1	24.2
1	1	14	27.1	28.5
1	1	16	24.3	25.7
1	1	18	35.0	36.1
1	1	20	32.5	35.1
1	2	1	51.0	53.0
1	2	3	54.4	51.8
1	2	5	52.6	50.2
1	2	7	98.7	92.9
1	2	9	47.3	47.3
1	2	11	117.1	106.6
1	2	13	62.3	64.1
1	2	15	64.3	64.3
1	2	17	14.8	23.2
1	2	19	17.8	16.0
1	3	0	28.0	26.3
1	3	2	22.0	29.3
1	3	4	57.2	67.6
1	3	6	29.1	31.9
1	3	8	81.0	90.6
1	3	10	55.6	59.1
1	3	12	131.4	137.0
1	3	14	87.0	89.6
1	3	16	73.9	72.3
1	3	18	17.2	17.2
1	3	20	14.3	13.8
1	4	1	97.8	93.3
1	4	3	231.4	221.6
1	4	5	175.8	183.3
1	4	7	34.9	33.0
1	4	9	60.2	66.9
1	4	11	49.0	51.7
1	4	13	147.3	135.8
1	4	15	31.9	31.6
1	4	17	74.6	66.4
1	4	19	19.5	19.4
1	4	21	15.6	11.8
1	5	2	22.4	21.7
1	5	4	22.0	24.1
1	5	6	20.9	17.2
1	5	8	13.3	12.4
1	5	10	13.0	15.5
1	5	12	17.8	20.5
1	5	14	17.0	19.8
1	5	16	28.1	24.1
1	5	18	16.0	17.7
1	5	20	25.6	25.9
1	6	1	20.4	19.3
1	6	3	31.4	33.1
1	6	5	94.8	96.0
1	6	7	28.8	30.1
1	6	9	23.5	17.1
1	6	11	20.6	19.9
1	6	13	34.8	30.8
1	6	15	9.7	4.6
1	6	17	15.8	10.2
1	6	19	33.5	35.8
1	6	21	10.8	14.4
1	7	2	44.1	42.0
1	7	4	14.2	12.1
1	7	6	50.2	49.0
1	7	8	31.4	29.5
1	7	10	61.2	61.2
1	7	12	23.3	23.5
1	7	14	34.8	30.8
1	7	16	9.7	4.6
1	7	18	15.8	10.2
1	7	20	33.5	35.8
1	8	1	10.8	14.4
1	8	3	44.1	42.0
1	8	5	14.2	12.1
1	8	7	50.2	49.0
1	8	9	31.4	29.5
1	8	11	61.2	61.2
1	8	13	23.3	23.5
1	8	15	34.8	30.8
1	8	17	9.7	4.6
1	8	19	15.8	10.2
1	8	21	33.5	35.8
1	9	2	10.8	14.4
1	9	4	44.1	42.0
1	9	6	14.2	12.1
1	9	8	50.2	49.0
1	9	10	31.4	29.5
1	9	12	61.2	61.2
1	9	14	23.3	23.5
1	9	16	34.8	30.8
1	9	18	9.7	4.6
1	9	20	15.8	10.2
1	10	1	33.5	35.8
1	10	3	10.8	14.4
1	10	5	44.1	42.0
1	10	7	14.2	12.1
1	10	9	50.2	49.0
1	10	11	31.4	29.5
1	10	13	61.2	61.2
1	10	15	23.3	23.5
1	10	17	34.8	30.8
1	10	19	9.7	4.6
1	10	21	15.8	10.2
1	11	2	33.5	35.8
1	11	4	10.8	14.4
1	11	6	44.1	42.0
1	11	8	14.2	12.1
1	11	10	50.2	49.0
1	11	12	31.4	29.5
1	11	14	61.2	61.2
1	11	16	23.3	23.5
1	11	18	34.8	30.8
1	11	20	9.7	4.6
1	12	1	15.8	10.2
1	12	3	33.5	35.8
1	12	5	10.8	14.4
1	12	7	44.1	42.0
1	12	9	14.2	12.1
1	12	11	50.2	49.0
1	12	13	31.4	29.5
1	12	15	61.2	61.2
1	12	17	23.3	23.5
1	12	19	34.8	30.8
1	12	21	9.7	4.6
1	13	2	15.8	10.2
1	13	4	33.5	35.8
1	13	6	10.8	14.4
1	13	8	44.1	42.0
1	13	10	14.2	12.1
1	13	12	50.2	49.0
1	13	14	31.4	29.5
1	13	16	61.2	61.2
1	13	18	23.3	23.5
1	13	20	34.8	30.8
1	14	1	9.7	4.6
1	14	3	15.8	10.2
1	14	5	33.5	35.8
1	14	7	10.8	14.4
1	14	9	44.1	42.0
1	14	11	14.2	12.1
1	14	13	50.2	49.0
1	14	15	31.4	29.5
1	14	17	61.2	61.2
1	14	19	23.3	23.5
1	14	21	34.8	30.8
1	15	2	9.7	4.6
1	15	4	15.8	10.2
1	15	6	33.5	35.8
1	15	8	10.8	14.4
1	15	10	44.1	42.0
1	15	12	14.2	12.1
1	15	14	50.2	49.0
1	15	16	31.4	29.5
1	15	18	61.2	61.2
1	15	20	23.3	23.5
1	16	1	34.8	30.8
1	16	3	9.7	4.6
1	16	5	15.8	10.2
1	16	7	33.5	35.8
1	16	9	10.8	14.4
1	16	11	44.1	42.0
1	16	13	14.2	12.1
1	16	15	50.2	49.0
1	16	17	31.4	29.5
1	16	19	61.2	61.2
1	16	21	23.3	23.5
1	17	2	34.8	30.8
1	17	4	9.7	4.6
1	17	6	15.8	10.2
1	17	8	33.5	35.8
1	17	10	10.8	14.4
1	17	12	44.1	42.0
1	17	14	14.2	12.1
1	17	16	50.2	49.0
1	17	18	31.4	29.5
1	17	20	61.2	61.2
1	18	1	23.3	23.5
1	18	3	34.8	30.8
1	18	5	9.7	4.6
1	18	7	15.8	10.2
1	18	9	33.5	35.8
1	18	11	10.8	14.4
1	18	13	44.1	42.0
1	18	15	14.2	12.1
1	18	17	50.2	49.0
1	18	19	31.4	29.5
1	18	21	61.2	61.2
1	19	2	23.3	23.5
1	19	4	34.8	30.8
1	19	6	9.7	4.6
1	19	8	15.8	10.2
1	19	10	33.5	35.8
1	19	12	10.8	14.4
1	19	14	44.1	42.0
1	19	16	14.2	12.1
1	19	18	50.2	49.0
1	19	20	31.4	29.5
1	20	1	61.2	61.2
1	20	3	23.3	23.5
1	20	5	34.8	30.8
1	20	7	9.7	4.6
1	20	9	15.8	10.2
1	20	11	33.5	35.8
1	20	13	10.8	14.4
1	20	15	44.1	42.0
1	20	17	14.2	12.1
1	20	19	50.2	49.0
1	20	21	31.4	29.5
2	0	0	202.4	193.3
2	0	2	19.1	14.4
2	0	4	42.0	41.9
2	0	6	19.0	19.4
2	0	8	47.4	48.3
2	0	10	19.0	17.5
2	0	12	48.4	48.3
2	0	14	61.8	61.0
2	0	16	19.0	19.4
2	0	18	47.4	48.3
2	0	20	19.0	17.5
2	1	1	9.9	9.9
2	1	3	48.4	48.3
2	1	5	61.8	61.0
2	1	7	19.0	19.4
2	1	9	47.4	48.3
2	1	11	19.0	17.5
2	1	13	48.4	48.3
2	1	15	61.8	61.0
2	1	17	19.0	19.4
2	1	19	47.4	48.3
2	1	21	19.0	17.5
2	2	2	51.0	53.0
2	2	4	54.4	51.8
2	2	6	52.6	50.2
2	2	8	98.7	92.9
2	2	10	47.3	47.3
2	2	12	117.1	106.6
2	2	14	62.3	64.1
2	2	16	64.3	64.3
2	2	18	14.8	23.2
2	2	20	17.8	16.0
2	3	1	28.0	26.3
2	3	3	22.0	29.3
2	3	5	57.2	67.6
2	3	7	29.1	31.9
2	3	9	81.0	90.6
2	3	11	55.6	59.1
2	3	13	131.4	137.0
2	3	15	87.0	89.6
2	3	17	73.9	72.3
2	3	19	17.2	17.2
2	3	21	14.3	13.8
2	4	2	97.8	93.3
2	4	4	231.4	221.6
2	4	6	175.8	183.3
2	4	8	34.9	33.0
2	4	10	60.2	66.9
2	4	12	49.0	51.7
2	4	14	147.3	135.8
2	4	16	31.9	31.6
2	4	18	74.6	66.4
2	4	20	19.5	19.4
2	5	1	15.6	11.8
2	5	3	22.4	21.7
2	5	5	22.0	24.1
2	5	7	20.9	17.2
2	5	9	13.3	12.4
2	5	11	13.0	15.5
2	5	13	17.8	20.5
2	5	15	17.0	19.8
2	5	17	28.1	24.1
2	5	19	16.0	17.7
2	5	21	25.6	25.9
2	6	2	20.4	19.3
2	6	4	31.4	33.1
2	6	6	94.8	96.0
2	6	8	28.8	30.1
2	6	10	23.5	17.1
2	6	12	20.6	19.9
2	6	14	34.8	30.8
2	6	16	9.7	4.6
2	6	18	15.8	10.2
2	6	20	33.5	35.8
2	7	1	10.8	14.4
2	7	3	44.1	42.0
2	7	5	14.2	12.1
2	7	7	50.2	49.0
2	7	9	31.4	29.5
2	7	11	61.2	61.2
2	7	13	23.3	23.5
2	7	15	34.8	30.8
2	7	17	9.7	4.6
2	7	19	15.8	10.2
2	7	21	33.5	35.8
2	8	2	10.8	14.4
2	8	4	44.1	42.0
2	8	6	14.2	12.1
2	8	8	50.2	49.0
2	8	10	31.4	29.5
2	8	12	61.2	61.2
2	8	14	23.3	23.5
2	8	16	34.8	30.8
2	8	18	9.7	4.6
2	8	20	15.8	10.2
2	9	1	33.5	35.8
2	9	3	10.8	14.4
2	9	5	44.1	42.0
2	9	7	14.2	12.1
2	9	9	50.2	49.0
2	9	11	31.4	29.5
2	9	13	61.2	61.2
2	9	15	23.3	23.5
2	9	17	34.8	30.8
2	9	19	9.7	4.6
2	9	21	15.8	10.2
2	10	2	33.5	35.8
2	10	4	10.8	14.4
2	10	6	44.1	42.0
2	10	8	14.2	12.1
2	10	10	50.2	49.0
2	10	12	31.4	29.5
2	10	14	61.2	61.2
2	10	16	23.3	23.5
2	10	18	34.8	30.8
2	10	20	9.7	4.6
2	11	1	15.8	10.2
2	11	3	33.5	35.8
2	11	5	10.8	14.4
2	11	7	44.1	42.0
2	11	9	14.2	12.1
2	11	11	50.2	49.0
2	11	13	31.4	29.5
2	11	15	61.2	61.2
2	11	17	23.3	23.5
2	11	19	34.8	30.8
2	11	21	9.7	4.6
2	12	2	15.8	10.2
2	12	4	33.5	35.8
2	12	6	10.8	14.4
2	12	8	44.1	42.0
2	12	10	14.2	12.1
2	12	12	50.2	49.0
2	12	14	31.4	29.5
2	12	16	61.2	61.2
2	12	18	23.3	23.5
2	12	20	34.8	30.8
2	13	1	9.7	4.6
2	13	3	15.8	10.2
2	13	5	33.5	35.8
2	13	7	10.8	14.4
2	13	9	44.1	42.0
2	13	11	14.2	12.1
2	13	13	50.2	49.0
2	13	15	31.4	29.5
2	13	17	61.2	61.2
2	13	19	23.3	23.5
2	13	21	34.8	30.8
2	14	2	9.7	4.6
2	14	4	15.8	10.2
2	14	6	33.5	35.8
2	14	8	10.8	14.4
2	14	10	44.1	42.0
2	14	12	14.2	12.1
2	14	14	50.2	49.0
2	14	16	31.4	29.5
2	14	18	61.2	61.2
2	14	20	23.3	23.5
2	15	1	34.8	30.8
2	15	3	9.7	4.6
2	15	5	15.8	10.2
2	15	7	33.5	35.8
2	15	9	10.8	14.4
2	15	11	44.1	42.0
2	15	13	14.2	12.1
2	15	15	50.2	49.0
2	15	17	31.4	29.5
2	15	19	61.2	61.2
2	15	21	23.3	23.5
2	16	2	34.8	30.8
2	16	4	9.7	4.6
2	16	6	15.8	10.2
2	16	8	33.5	35.8
2	16	10	10.8	14.4
2	16	12	44.1	42.0
2	16	14	14.2	12.1
2	16	16	50.2	49.0
2	16	18	31.4	29.5
2	16	20	61.2	61.2
2	17	1	23.3	23.5
2	17	3	34.8	30.8
2	17	5	9.7	4.6
2	17	7	15.8	10.2
2	17	9	33.5

H	K	L	F OBS	F CALC
-6	6	19	11.7	-4.1
-6	6	17	19.5	-19.5
-6	6	15	25.9	27.7
-6	6	14	21.2	-22.0
-6	6	12	29.1	25.9
-6	6	11	40.4	39.9
-6	6	9	64.6	-64.5
-6	6	7	55.0	54.2
-6	6	6	36.0	-34.7
-6	6	4	46.4	-44.5
-6	6	3	49.3	45.2
-6	6	2	28.0	29.5
-6	6	1	29.9	-32.7
-6	6	0	79.6	-83.9
-6	4	22	12.8	-11.4
-6	4	20	19.1	9.1
-6	4	19	15.1	15.2
-6	4	18	16.9	-17.5
-6	4	17	34.0	-37.5
-6	4	16	22.6	23.3
-6	4	15	34.4	37.2
-6	4	14	28.4	-32.0
-6	4	13	35.3	-32.6
-6	4	12	32.6	28.4
-6	4	11	36.3	35.3
-6	4	9	44.9	-41.1
-6	4	7	79.7	-77.0
-6	4	6	67.9	61.4
-6	4	5	48.6	71.4
-6	4	4	40.3	-40.7
-6	4	3	54.4	-49.1
-6	4	2	22.0	12.4
-6	4	1	38.1	11.6
-6	4	0	30.9	-33.7
-6	2	16	48.1	52.2
-6	2	14	45.8	44.3
-6	2	13	31.6	23.4
-6	2	12	60.6	62.2
-6	2	11	29.2	25.1
-6	2	10	46.7	46.7
-6	2	9	30.2	31.6
-6	2	8	79.2	82.5
-6	2	6	74.4	76.0
-6	2	5	33.6	34.7
-6	2	4	112.1	112.4
-6	2	3	31.7	30.1
-6	2	2	114.5	-114.5
-6	2	1	44.7	48.5
-6	0	24	17.1	15.0
-6	0	22	12.1	13.3
-6	0	20	24.0	28.0
-6	0	18	30.5	28.9
-6	0	16	37.6	35.8
-6	0	14	49.7	48.1
-6	0	12	88.1	86.4
-6	0	10	62.2	61.7
-6	0	8	89.0	90.1
-6	0	6	114.5	-112.3
-6	0	4	95.7	105.0
-6	0	2	122.9	-126.3
-7	11	11	13.4	11.4
-7	11	10	21.8	19.8
-7	11	9	14.1	11.4
-7	11	8	16.3	21.7
-7	11	7	21.3	17.1
-7	11	5	16.7	14.7
-7	11	4	23.7	20.7
-7	11	2	25.9	23.0
-7	9	17	13.6	13.7
-7	9	15	26.5	20.1
-7	9	14	11.2	7.4
-7	9	11	29.6	28.4
-7	9	10	11.4	12.1
-7	9	9	23.2	25.1
-7	9	7	27.6	23.0
-7	9	6	16.2	11.2
-7	9	5	30.4	33.7
-7	9	4	11.0	8.4
-7	9	3	29.7	31.9
-7	9	1	32.0	34.1
-7	7	18	12.6	6.2
-7	7	17	21.9	19.4
-7	7	15	23.2	24.2
-7	7	13	24.2	24.2
-7	7	12	12.2	12.4
-7	7	11	42.9	41.5
-7	7	10	21.6	21.6
-7	5	19	18.4	19.4
-7	5	17	20.4	23.1
-7	5	16	23.4	24.1
-7	5	15	33.7	34.4
-7	5	14	42.9	41.5
-7	5	13	19.2	19.4
-7	5	12	44.1	45.8
-7	5	11	26.1	27.5
-7	5	10	11.4	12.1
-7	5	9	23.2	25.1
-7	5	7	27.6	23.0
-7	5	6	16.2	11.2
-7	5	5	30.4	33.7
-7	5	4	11.0	8.4
-7	5	3	29.7	31.9
-7	5	1	32.0	34.1
-7	3	19	18.4	19.4
-7	3	17	20.4	23.1
-7	3	16	23.4	24.1
-7	3	15	33.7	34.4
-7	3	14	42.9	41.5
-7	3	13	19.2	19.4
-7	3	12	44.1	45.8
-7	3	11	26.1	27.5
-7	3	10	11.4	12.1
-7	3	9	23.2	25.1
-7	3	7	27.6	23.0
-7	3	6	16.2	11.2
-7	3	5	30.4	33.7
-7	3	4	11.0	8.4
-7	3	3	29.7	31.9
-7	3	1	32.0	34.1
-7	1	19	18.4	19.4
-7	1	17	20.4	23.1
-7	1	16	23.4	24.1
-7	1	15	33.7	34.4
-7	1	14	42.9	41.5
-7	1	13	19.2	19.4
-7	1	12	44.1	45.8
-7	1	11	26.1	27.5
-7	1	10	11.4	12.1
-7	1	9	23.2	25.1
-7	1	7	27.6	23.0
-7	1	6	16.2	11.2
-7	1	5	30.4	33.7
-7	1	4	11.0	8.4
-7	1	3	29.7	31.9
-7	1	1	32.0	34.1
-8	8	16	27.9	29.9
-8	8	14	49.4	45.5
-8	8	12	77.7	78.9
-8	8	10	80.7	-80.6
-8	8	8	65.6	64.8
-8	8	6	69.9	-73.0
-8	8	4	122.5	131.3
-8	8	2	88.7	-93.3
-8	8	0	89.0	84.6
-9	11	9	19.0	-12.1
-9	11	8	23.4	-13.9
-9	11	6	23.2	14.2
-9	9	16	17.6	-14.3
-9	9	15	18.4	15.9
-9	9	13	29.2	-32.4
-9	9	12	13.6	-10.8
-9	9	11	22.9	21.5
-9	9	9	27.0	-27.9
-9	9	7	20.1	26.6
-9	9	6	18.6	13.5
-9	9	5	22.8	-25.8
-9	9	3	20.7	24.6
-9	9	1	11.9	-14.2
-9	7	17	13.8	-16.9
-9	7	15	25.3	21.9
-9	7	13	25.9	-25.6
-9	7	11	34.5	33.9
-9	7	10	45.3	-43.7
-9	7	9	39.8	40.0
-9	7	7	35.4	-40.0
-9	7	5	49.1	49.1
-9	7	3	33.2	32.3
-9	7	1	48.7	-51.2
-9	5	15	23.3	-23.8
-9	5	13	22.6	20.9
-9	5	11	34.5	-37.8
-9	5	9	28.2	-32.8
-9	5	7	43.4	44.3
-9	5	5	21.3	-22.0
-9	5	3	32.3	-34.3
-9	5	1	39.7	39.7
-9	3	17	10.2	-14.2
-9	3	16	13.1	15.4
-9	3	15	19.1	18.5
-9	3	14	48.1	-44.1
-9	3	13	41.8	-41.9
-9	3	12	46.5	48.0
-9	3	11	32.2	26.8
-9	3	10	26.1	-27.7
-9	3	9	28.1	-29.4
-9	3	7	39.1	39.1
-9	3	6	37.1	31.4
-9	3	4	37.0	-37.6
-9	3	3	37.7	-37.6
-9	3	2	39.7	42.4
-9	3	1	29.8	-30.8
-9	1	19	19.4	-19.4
-9	1	17	25.1	-20.9
-9	1	16	24.3	17.1
-9	1	15	22.3	27.5
-9	1	14	42.4	-40.8
-9	1	12	41.1	-39.7
-9	1	11	51.8	-47.9
-9	1	10	37.4	-37.3
-9	1	9	32.3	31.5
-9	1	7	32.4	-32.1
-9	1	6	31.4	-37.8
-9	1	5	38.8	-37.3
-9	1	4	34.7	34.9
-9	1	3	27.7	28.0
-9	1	2	14.4	20.3
-9	1	1	31.4	-37.8
-10	10	12	15.1	-15.1
-10	10	11	16.1	16.4
-10	10	9	18.6	-16.0
-10	10	8	19.5	19.1
-10	10	7	17.2	14.2
-10	10	5	17.4	17.4
-10	10	4	13.1	14.0
-10	10	3	16.3	13.4
-10	10	2	17.4	20.6
-10	10	1	12.2	14.4
-10	8	18	15.4	3.4
-10	8	17	16.4	-11.0
-10	8	16	10.9	-4.8
-10	8	15	19.5	19.1
-10	8	13	24.7	-19.8
-10	8	12	12.9	-9.8
-10	8	11	22.9	21.9
-10	8	9	29.9	-26.3
-10	8	8	24.1	19.8
-10	8	7	20.0	-19.9
-10	8	6	16.4	-12.1
-10	8	4	16.0	-12.1
-10	6	3	20.1	23.6
-10	6	2	13.4	-11.7
-10	6	0	19.8	22.3
-10	4	19	12.3	6.5
-10	4	17	27.6	-31.8
-10	4	15	31.3	34.1
-10	4	14	12.0	-20.8
-10	4	13	34.0	-22.8
-10	4	12	39.9	34.7
-10	4	11	24.0	24.5
-10	4	10	23.6	-27.5
-10	4	9	35.9	-33.2
-10	4	8	24.6	30.4
-10	4	7	50.0	52.0
-10	4	6	37.0	-37.0
-10	4	5	39.6	-39.4
-10	4	4	29.8	27.5
-10	4	3	25.6	24.2
-10	4	2	39.8	-43.2
-10	4	1	28.9	-31.6
-10	2	22	20.2	-12.5
-10	2	20	19.6	14.7
-10	2	18	17.2	-14.6
-10	2	17	19.4	-16.9
-10	2	16	20.3	22.2
-10	2	15	19.8	19.8
-10	2	14	34.9	-34.6
-10	2	12	46.2	42.7
-10	2	11	29.0	24.4
-10	2	10	45.3	43.7
-10	2	9	26.3	-29.9
-10	2	8	49.1	49.1
-10	2	7	33.2	32.3
-10	2	6	48.7	-51.2
-10	2	5	23.3	-23.8
-10	2	4	22.6	20.9
-10	2	3	34.5	37.8
-10	2	2	28.2	-32.8
-10	2	1	19.4	-16.1
-10	0	24	17.9	10.4
-10	0	22	23.0	-20.2
-10	0	20	24.0	20.2
-10	0	18	39.1	-39.0
-10	0	16	47.8	43.9
-10	0	14	41.0	-36.7
-10	0	12	54.0	57.1
-10	0	10	69.0	-70.5
-10	0	8	77.6	79.6
-10	0	6	68.1	-70.1
-10	0	4	79.0	81.7
-10	0	2	71.6	-75.7
-11	9	15	18.9	12.9
-11	9	12	16.0	15.8
-11	9	11	23.6	19.0
-11	9	9	24.2	-20.6
-11	9	7	21.2	21.6
-11	9	5	15.3	-18.0
-11	9	3	16.2	20.1
-11	9	2	14.1	8.5
-11	7	19	11.7	-10.8
-11	7	18	12.0	10.4
-11	7	17	19.6	11.4
-11	7	15	20.0	19.2
-11	7	13	20.9	-18.5
-11	7	12	14.5	6.3
-11	7	11	29.2	23.9
-11	7	10	12.6	-9.8
-11	7	9	24.6	25.1
-11	7	7	23.6	27.3
-11	7	6	12.2	5.6
-11	7	5	29.6	-31.8
-11	7	3	25.4	29.1
-11	7	1	23.8	-22.3
-11	5	21	14.0	8.1
-11	5	20	14.6	8.1
-11	5	19	13.9	10.4
-11	5	18	12.0	8.3
-11	5	17	20.2	16.5
-11	5	16	15.0	10.0
-11	5	15	19.5	16.3
-11	5	13	14.6	11.0
-11	5	12	25.0	22.9
-11	5	11	23.6	18.1
-11	5	10	22.2	23.9
-11	5	9	19.3	18.2
-11	5	7	29.9	24.4
-11	5	6	18.0	13.4
-11	5	5	21.5	25.4
-11	5	4	22.5	21.0
-11	5	3	26.3	26.2
-11	5	2	22.6	17.9
-11	5	1	24.2	20.7
-11	3	19	18.2	16.4
-11	3	17	18.2	16.4
-11	3	16	13.1	14.0
-11	3	15	22.2	20.3
-11	3	14	20.9	21.1
-11	3	13	22.4	19.2
-11	3	12	18.2	21.2
-11	3	11	20.4	20.4
-11	3	10	32.2	33.1
-11	3	9	34.0	35.7
-11	3	7	35.4	34.7
-11	3	6	37.2	31.3
-11	3	5	19.6	22.5
-11	3	4	17.0	11.7
-11	3	2	39.2	42.2
-11	1	1	26.7	30.3
-11	1	23	11.6	0.4
-11	1	20	14.9	14.0
-11	1	18	25.8	19.7
-11	1	16	26.3	28.7
-11	1	15	12.0	9.1
-11	1	14	27.7	25.1
-11	1	12	16.3	22.2
-11	1	11	16.8	13.0
-11	1	10	34.5	33.2
-11	1	8	51.0	53.9
-11	1	6	40.9	40.4
-11	1	4	16.8	24.7
-11	1	3	9.9	3.5
-11	1	2	29.0	29.0
-11	1	0	20.6	24.9
-12	12	13	17.9	21.4
-12	12	9	17.9	16.4
-12	12	8	23.7	19.2
-12	12	7	19.7	19.9
-12	12	6	18.8	21.4
-12	12	5	23.7	22.4
-12	12	4	21.8	20.6
-12	12	3	19.4	18.2
-12	12	2	20.6	20.4
-12	12	1	19.2	19.8
-12	10	12	14.1	13.6
-12	10	11	16.4	16.4
-12	10	10	20.4	20.4
-12	10	9	19.4	19.4
-12	10	8	19.2	19.2
-12	10	7	19.2	19.2
-12	10	6	19.2	19.2
-12	10	5	19.2	19.2
-12	10	4	19.2	19.2
-12	10	3	19.2	19.2
-12	10	2	19.2	19.2
-12	10	1	19.2	19.2
-12	8	13	20.7	18.7
-12	8	12	21.2	18.0
-12	8	11	18.8	20.6
-12	8	10	29.2	27.1
-12	8	9	19.2	19.2
-12	8	8	20.0	19.9
-12	8	7	21.1	19.9
-12	8	6	24.5	23.6
-12	8	5	22.8	20.7
-12	8	4	17.3	24.4
-12	8	3	21.0	19.3
-12	8	2	23.2	23.4
-12	8	1	26.4	24.3
-12	6	13	20.3	19.2
-12	6	11	14.9	14.0
-12	6	9	25.8	19.7
-12	6	8	26.3	28.7
-12	6	7	12.0	9.1
-12	6	6	27.7	25.1
-12	6	5	16.3	22.2
-12	6	4	16.8	13.0
-12	6	3	34.5	33.2
-12	6	2	51.0	53.9
-12	6	1	40.9	40.4
-12	6	0	26.7	30.3
-12	4	19	11.6	0.4
-12	4	17	14.9	14.0
-12	4	15	25.8	19.7
-12	4	14	26.3	28.7
-12	4	13	12.0	9.1
-12	4	12	27.7	25.1
-12	4	11	16.3	22.2
-12	4	10	16.8	13.0
-12	4	9	34.5	33.2
-12	4	8	51.0	53.9
-12	4	7	40.9	40.4
-12	4	6	26.7	30.3
-12	4	5	16.8	24.7
-12	4	4	9.9	3.5
-12	4	3	29.0	29.0
-12	4	1	20.6	24.9
-12	2	19	17.9	21.4
-12	2	15	17.9	16.4
-12	2	14	23.7	19.2
-12	2	13	19.7	19.9
-12	2	12	18.8	21.4
-12	2	11	23.7	22.4
-12	2	10	21.8	20.6
-12	2	9	19.4	18.2
-12	2	8	20.6	20.4
-12	2	7	19.2	19.8
-12	2	6	14.1	13.6
-12	2	5	16.4	16.4
-12	2	4	20.4	20.4
-12	2	3	19.4	19.4
-12	2	2	19.2	19.2
-12	2	1	19.2	19.2
-12	0	13	20.7	18.7
-12	0	12	21.2	18.0
-12	0	11	18.8	20.6
-12	0	10	29.2	27.1
-12	0	9	19.2	19.2
-12	0	8	20.0	19.9
-12	0	7	21.1	19.9
-12	0	6	24.5	23.6
-12	0	5	22.8	20.7
-12	0	4	17.3	24.4
-12	0	3	21.0	19.3
-12	0	2	23.2	23.4
-12	0	1	26.4	24.3
-13	9	2	23.2	-19.0
-13	9	1	13.4	-13.6
-13	7	20	22.8	13.0
-13	7	18	23.6	-19.7
-13	7	16	23.7	-19.0
-13	7	14	15.8	-10.6
-13	7	13	11.3	10.7
-13	7	12	11.3	9.1
-13	7	10	16.8	16.4
-13	7	9	22.8	-17.0
-13	7	8	19.7	16.9
-13	7	7	11.8	13.5
-13	7	6	14.6	12.8
-13	7	5	14.6	14.3
-13	7	4	16.4	16.4
-13	7	3	20.4	20.4
-13	7	2	19.4	19.4
-13	7	1	19.2	19.2
-13	5	21	13.0	10.2
-13	5	20	14.6	14.2
-13	5	19	13.2	12.2
-13	5	18	17.9	15.2
-13	5	17	17.3	14.1
-13	5	16	20.6	21.0
-13	5	15	19.6	16.3
-13	5	14	15.2	12.4
-13	5	13	19.2	18.7
-13	5	12	19.6	19.2
-13	5	11	24.1	19.8
-13	5	10	20.0	19.9
-13	5	9	22.8	20.7
-13	5	8	19.7	16.9
-13	5	7	11.8	13.5
-13	5	6	14.6	12.8
-13	5	5	14.6	14.3
-13	5	4	16.4	16.4
-13	5	3	20.4	20.4
-13	5	2	19.4	19.4
-13	5	1	19.2	19.2
-13	3	19	13.2	12.6
-13	3	18	15.2	12.6
-13	3	17	17.7	14.2
-13	3	16	15.4	12.6
-13	3	15	18.2	16.4
-13	3	14	20.9	16.4
-13	3	13	22.4	19.2
-13	3	12	18.2	21.2
-13	3	11	20.4	20.4
-13	3	10	32.2	33.1
-13	3	9	34.0	35.7
-13	3	8	35.4	34.7
-13	3	7	37.2	31.3
-13	3	6	19.6	22.5
-13	3	5	15.2	17.1
-13	3	4	17.0	11.7
-13	3	3	39.2	42.2
-13	1	21	11.6	0.4
-13	1	19	14.9	14.0
-13	1	17	25.8	19.7
-13	1	16	26.3	28.7
-13	1	15	12.0	9.1
-13	1	13	27.7	25.1
-13	1	12	16.3	22.2
-13	1	10	16.8	13.0
-13	1	9	34.5	33.2
-13	1	7	51.0	53.9
-13	1	6	40.9	40.4
-13	1	4	16.8	24.7
-13	1	3	9.9	3.5
-13	1	1	29.0	29.0
-14	6	18	12.0	10.2
-14	6	16	14.9	14.0
-14	6	14	25.8	19.7
-14	6	13	26.3	28.7
-14	6	11	12.0	9.1
-14	6	9	27.7	25.1
-14	6	8	16.3	22.2
-14	6	6	34.5	33.2
-14	6	4	51.0	53.9
-14	6	3	40.9	40.4
-14	6	1	26.7	30.3
-14	4	20	11.6	0.4
-14	4	18	14.9	14.0
-14	4	16	25.8	19.7
-14	4	15	26.3	28.7
-14	4	14	12.0	9.1
-14	4	12	27.7	25.1
-14	4	11	16.3	22.2
-14	4	10	16.8	13.0
-14	4	8	34.5	33.2
-14	4	6	51.0	53.9
-14	4	5	40.9	40.4
-14	4	3	16.8	24.7
-14	4	2	9.9	3.5
-14	4	0	29.0	29.0
-14	2	17	13.2	12.6
-14	2	16	15.2	12.6
-14	2	15	17.7	14.2
-14	2	14	15.4	12.6
-14	2	13	18.2	16.4
-14	2	12	20.9	16.4
-14	2	11	22.4	19.2
-14	2	10	18.2	21.2
-14	2	9	20.4	20.4
-14	2	8	32.2	33.1
-14	2	7	34.0	35.7
-14	2	6	35.4	34.7
-14	2	5	37.2	31.3
-14	2	4	19.6	22.5
-14	2	3	15.2	17.1
-14	2	2	17.0	11.7
-14	2	1	39.2	42.2
-14	0	19	11.6	0.4
-14	0	17	14.9	14.0
-14	0	15	25.8	19.7
-14	0	14	26.3	28.7
-14	0	12	12.0	9.1
-14	0	10	27.7	25.1
-14	0	9	16.3	22.2
-14	0	7	34.5	33.2
-14	0	5	51.0	53.9
-14	0	4	40.9	40.4
-14	0	2	16.8	24.7
-14	0	1	9.9	3.5
-14	0	0	29.0	29.0
-15	6	14	12.2	6.5
-15	6	13	27.6	31.8
-15	6	11	37.6	38.4
-15	6	9	32.5	29.5
-15	6	7	39.1	45.9
-15	6	5	48.3	49.4
-15	6	4	10.6	6.4
-15	6	3	24.0	24.5
-15	6	2	23.6	27.5
-15	6	1	17.9	17.0
-15	4	16	17.9	14.1
-15	4	15	31.3	34.1
-15	4	14	12.0	20.8
-15	4	13	34.0	22.8
-15	4	12	39.9	34.7
-15	4	11	24.0	24.5
-15	4	10	23.6	27.5
-15	4	9	35.9	33.2
-15	4	8	24.6	30.4
-15	4	7	50.0	52.0
-15	4	6	37.0	37.0
-15	4	5	39.6	39.4
-15	4	4	29.8	27.5
-15	4	3	25.6	24.2
-15	4	2	39.8	43.2
-15	4	1	28.9	31.6
-15	2	22	20.2	12.5
-15	2	20	19.6	14.7
-15	2	18	17.2	14.6
-15	2	17	19.4	16.9
-15	2	16	20.3	22.2
-15	2	15	19.8	19.8
-15	2	14	34.9	34.6
-15	2	12	46.2	42.7
-15	2	11	29.0	24.4
-15	2	10	45.3	43.7
-15	2	9	26.3	29.9
-15	2	8	49.1	49.1
-15	2	7	33.2	32.3
-15	2	6	48.7	51.2
-15	2	5	23.3	23.8
-15	2	4	22.6	20.9
-15	2	3	34.5	37.8
-15	2	2	28.2	32.8
-15	2	1	19.4

TABLE 23

$Cd(py)_3(NO_3)_2$

Atom positions (fractional coordinates)

	x/a	y/b	z/c
Cd	0.5	0.53497(11)	0.25
C(1)	0.2878(14)	0.4667(16)	0.0662(8)
C(2)	0.1844(16)	0.4794(18)	-0.0061(9)
C(3)	0.1138(14)	0.5950(17)	-0.0143(9)
C(4)	0.1473(12)	0.6984(15)	0.0486(8)
C(5)	0.2554(11)	0.6773(14)	0.1193(8)
C(6)	0.4130(12)	0.2169(13)	0.2578(9)
C(7)	0.3135(13)	0.0691(14)	0.2584(10)
C(8)	0.5	-0.0010(17)	0.25
O(1)	0.4237(9)	0.7126(10)	0.3156(6)
O(2)	0.4025(10)	0.5003(10)	0.3474(7)
O(3)	0.3604(11)	0.6713(14)	0.4120(8)
N(1)	0.3247(9)	0.5649(10)	0.1297(6)
N(2)	0.3957(9)	0.6298(12)	0.3609(7)
N(3)	0.5	0.2878(19)	0.25

TABLE 24

$Cd(py)_3(NO_3)_2$

(a) Anisotropic temperature factors ($Å^2$) *

	U_{11}	U_{22}	U_{33}	$2U_{32}$	$2U_{31}$	$2U_{12}$
Cd	0.045	0.036	0.046	0.000	0.026	0.000
C(1)	0.080	0.064	0.048	-0.010	0.019	0.027
C(2)	0.088	0.073	0.053	0.009	0.001	0.041
C(3)	0.075	0.074	0.050	0.013	0.015	-0.024
C(4)	0.054	0.065	0.050	0.016	0.008	0.018
C(5)	0.051	0.053	0.057	0.006	0.030	0.010
C(6)	0.059	0.041	0.078	-0.003	0.067	-0.016
C(7)	0.068	0.049	0.081	0.002	0.070	-0.016
C(8)	0.077	0.038	0.059	0.000	0.017	0.000
O(1)	0.074	0.054	0.060	0.007	0.037	-0.013
O(2)	0.084	0.048	0.094	0.003	0.092	-0.002
O(3)	0.102	0.095	0.090	-0.076	0.119	-0.023
N(1)	0.049	0.046	0.047	0.009	0.032	0.017
N(2)	0.049	0.059	0.057	-0.021	0.029	-0.010
N(3)	0.074	0.038	0.059	0.000	0.044	0.000

(b) Mean estimated standard deviations ($Å^2$)

Cd	0.001	0.001	0.001	-	0.001	-
C	0.008	0.008	0.006	0.010	0.012	0.012
O	0.006	0.005	0.006	0.009	0.010	0.008
N	0.005	0.005	0.005	0.008	0.008	0.008

* These are the values of U_{ij} in equation (5) (Section I.1.4(b)).

APPENDIX VI

EXPERIMENTAL

DINITRATOBIS(α-PICOLINE)-COPPER(II), FORMS I & II

Preparation of Crystals

The complex $Cu(\alpha\text{-pic})_2(NO_3)_2$ was prepared according to the method of Lever [201], and recrystallised from methanol-2,2-dimethoxypropane (1:1) containing a little α-picoline. The isolation of two separate crystalline forms is dependent upon the temperature to which the crystallising liquid is heated before cooling [206]: if it is only warmed, crystals of Form (I) result, but, if it is boiled for several minutes, Form (II) crystals are obtained. The crystals were coated with collodion to prevent decomposition.

Crystal Data

$C_6H_7N_3O_6Cu$

M = 373.6

Form (I)

Monoclinic

$a = 8.31 \pm 0.03$, $b = 14.81 \pm 0.03$, $c = 14.14 \pm 0.03$ Å,

$\beta = 123.9 \pm 0.2^{\circ}$, $U = 1444$ Å^3

$D_m = 1.70$, $Z = 4$, $D_c = 1.72$

$F(000) = 764$

Space group $P2_1/c$ (C_{2h}^5, No 14) from systematic absences: $0k0$ when k odd, $h0\ell$ when ℓ odd.

Cu-K_α X-rays, $\lambda = 1.5418$ Å

μ(Cu-K_α) = 25.5 cm^{-1}

Form (II)

Monoclinic

$a = 8.57 \pm 0.03$, $b = 14.39 \pm 0.03$, $c = 14.20 \pm 0.03$ Å,

$\beta = 119.5 \pm 0.2^\circ$, $U = 1524$ $Å^3$

$D_m = 1.63$, $Z = 4$, $D_c = 1.63$

$F(000) = 764$

Space group $P2_1/c$ (C_{2h}^5, No 14) from systematic absences

μ (Cu-K_α) = 24.2 cm^{-1}

Crystallographic Measurements

The unit-cell parameters for both crystals were determined from oscillation and Weissenberg photographs taken with Cu-K_α radiation, and from precession photographs taken with Mo-K_α (λ = 0.7107 Å) radiation.

1134 independent reflections from the reciprocal-lattice nets 0-$6k\ell$ for Form (I) and 1341 from the nets 0-$7k\ell$ for Form (II), were recorded on equatorial and equi-inclination Weissenberg photographs by the multiple-film technique and were estimated visually by comparison with a calibrated strip. After correction for Lorentz, polarisation, and rotation factors, the structure amplitudes were placed on an overall scale by comparison with values

obtained from the h0ℓ reciprocal-lattice net recorded by precession methods. Unobserved reflections were not included in the calculations and absorption corrections were not applied.

Structure Determinations

Both structures were revealed by conventional Patterson and electron-density calculations with initial phasing appropriate to the respective copper atoms. Several cycles of structure-factor and electron-density calculations effected initial refinement which reduced the respective R values to 0.21 (Form I) and 0.20 (Form II). During these preliminary calculations an overall vibration parameter, U_{iso} (0.06 Å^2), was assigned to the atoms in each case.

Structure Refinement

The least-squares refinement of positional, anisotropic thermal, and scale parameters in each case converged after 10 cycles. For Form I, the final R was 0.116 and R' was 0.023. For Form II, the final R was 0.093 and R' was 0.016. Details of both refinements are given in Table 25. After the initial refinement, both sets of data were put on overall absolute scales and in the subsequent cycles these overall scale parameters were refined.

The refinement of anisotropic thermal parameters necessitated the use of the block-diagonal approximation to the normal-equation matrix because of computer-store limitations in both cases.

In all refinement cycles, a weighting scheme given as equation (32) (Section I.1.8(b)) was applied to the data. Initially the p parameters were chosen to give unit weights to all reflections, but they were varied in later cycles as indicated by a $|F_o|$ and $(\sin\theta/\lambda)$ analysis of $\sum w\Delta^2$. For Form I the final values are : p_1 50, p_2 0.1, p_3 0.0001, p_4 0; for Form II : p_1 50, p_2 0.01, p_3 0.0001, p_4 0.

At the conclusion of both refinements, difference syntheses and final electron-density distributions were evaluated and revealed no errors in the structures, although peaks identified from the difference synthesis were in positions stereochemically acceptable for hydrogen atoms. They were not included in the analysis.

In all the structure-factor calculations, the atomic scattering factors used are those given in ref. 212. Observed and calculated structure factors are listed in Tables 26 (Form I) and 27 (Form II). The fractional coordinates of all non-hydrogen atoms are given in Table 28 (Form I) and Table 30 (Form II) and the respective anisotropic thermal parameters are included

in Tables 29 (Form I) and 31 (Form II).

The relevant interatomic dimensions and some calculated least-squares best planes through the molecules are given in Section III.1.2. The estimated standard deviations recorded were derived from the inverse of the least-squares normal-equation matrix, and are probably best regarded as minimum values.

TABLE 25

Course of refinements

Parameters Refined	Form	Cycles	Final $\underline{R}$	Final $\underline{R}'$
$\underline{x}$, $\underline{y}$, $\underline{z}$, $\underline{U}_{iso}$ for Cu, N, 0, C; layer scale factors, unit weights, full matrix	I	1-3	0.149	0.040
	II	1-3	0.135	0.031
$\underline{x}$, $\underline{y}$, $\underline{z}$, $\underline{U}_{iso}$ for Cu, N, 0, C; layer scale factors, weighting scheme adjusted, full matrix	I	4-5	0.146	0.033
	II	4-6	0.130	0.026
$\underline{x}$, $\underline{y}$, $\underline{z}$, $\underline{U}_{ij}$ ($\underline{i}$, $\underline{j}$ = 1, 2, 3) for Cu, N, 0, C; overall scale, small adjustments to weighting scheme, Block diagonal approximation to normal equation matrix	I	6-10	0.116	0.021
	II	7-10	0.093	0.016

TABLE 26

$Cu(\alpha\text{-pic})_2(NO_3)_2$ - Form I

Observed and final-calculated structure amplitudes

H	K	L	F OBS	F CALC
0	0	12	21.5	-19.9
0	0	10	31.8	30.0
0	0	8	70.5	-73.7
0	0	4	36.9	44.7
0	1	13	17.8	23.6
0	1	11	27.1	-21.7
0	1	10	39.5	-32.1
0	1	9	22.2	19.5
0	1	8	40.0	36.0
0	1	7	30.2	-27.3
0	1	6	29.4	-21.6
0	1	5	14.8	20.9
0	1	4	36.3	49.7
0	1	3	26.0	-43.1
0	1	2	53.9	-66.7
0	2	11	11.4	-11.3
0	2	10	11.3	-10.3
0	2	9	15.2	14.7
0	2	8	19.3	-19.2
0	2	7	47.5	47.3
0	2	6	34.1	31.4
0	2	5	83.6	-74.9
0	2	4	12.3	-17.7
0	2	3	31.5	33.1
0	2	2	8.6	4.9
0	4	11	11.2	13.6
0	4	10	14.7	-15.4
0	4	8	39.5	-23.5
0	4	7	29.2	-25.0
0	4	6	30.3	37.5
0	4	5	10.2	13.1
0	4	4	13.1	4.3
0	4	2	51.8	53.1
0	4	1	127.9	152.1
0	5	12	5.9	-9.5
0	5	10	23.7	28.2
0	5	8	25.2	-24.9
0	5	6	15.9	-8.1
0	5	4	50.3	-49.3
0	5	1	11.4	-11.2
0	6	11	14.1	18.6
0	6	10	18.6	20.9
0	6	9	12.5	8.6
0	6	8	45.1	-59.2
0	6	5	11.4	8.1
0	6	4	39.5	41.8
0	6	2	122.0	-110.6
0	6	1	45.9	59.3
0	7	11	21.2	-21.2
0	7	10	19.5	-17.1
0	7	9	23.7	25.6
0	7	8	28.7	25.1
0	7	7	27.4	-24.0
0	7	6	29.4	-21.7
0	7	5	20.9	23.5
0	7	4	22.6	30.5
0	7	2	47.8	-49.7
0	7	1	17.0	-27.4
0	8	11	10.2	-12.2
0	8	9	27.9	14.8
0	8	7	27.0	23.4
0	8	6	20.9	16.5
0	8	5	51.1	-57.3
0	8	4	15.3	-15.9
0	8	3	10.3	12.0
0	8	2	14.9	14.9
0	8	1	136.4	-131.4
0	8	0	13.6	-12.4
0	9	11	13.6	15.9
0	9	9	11.9	-28.4
0	9	8	27.1	27.7
0	9	7	42.5	46.4
0	9	6	20.6	-18.2
0	9	5	52.9	-57.7
0	9	3	14.3	14.1
0	9	2	27.7	32.7
0	9	1	14.2	-18.1
0	10	10	19.3	15.4
0	10	9	25.5	-24.4
0	10	8	38.6	42.6
0	10	6	13.6	-14.7
0	10	5	21.3	-24.7
0	10	3	10.3	11.4
0	10	2	33.1	39.4
0	10	1	34.7	54.2
0	10	0	45.5	-101.7
0	11	10	14.3	15.4
0	11	9	25.5	-24.4
0	11	6	12.7	-8.9
0	11	5	10.3	11.6
0	11	2	15.0	11.7
C	12	6	24.5	-27.1
C	12	4	13.1	18.7
C	12	2	33.3	-42.9
C	12	1	39.6	38.5
C	12	0	65.2	66.4
C	13	7	30.2	-25.9
C	13	6	17.9	-16.6
C	13	5	33.8	31.3
C	13	4	11.4	13.7
C	13	3	18.6	-22.4
C	14	7	11.1	13.5
C	14	5	18.6	-21.9
C	14	3	17.1	20.6
C	14	1	45.2	-47.5
C	14	0	13.1	8.4
C	15	7	16.8	15.1
C	15	5	19.2	-13.7
C	15	4	13.4	11.6
C	15	3	10.7	10.1
C	15	2	15.4	-17.6
C	16	4	13.2	-17.7
C	16	3	11.2	-12.2
C	16	1	14.4	12.4
C	16	2	46.8	42.7
C	17	4	10.1	-10.1
C	18	2	17.1	-14.5
C	18	1	29.7	31.5
C	18	0	29.7	22.9
1	C	12	12.8	19.4
1	0	10	49.5	41.6
1	0	8	43.6	-46.1
1	0	6	67.3	59.9
1	0	4	45.9	-49.6
1	0	2	120.9	113.6
1	0	1	113.3	-98.6
1	0	0	19.4	13.9
1	1	11	63.6	-37.3
1	1	10	48.7	39.1
1	1	9	52.7	49.8
1	1	8	20.7	-21.1
1	1	7	7.5	11.4
1	1	6	29.7	-30.5
1	1	5	30.2	33.1
1	1	4	73.0	69.5
1	1	3	51.3	-52.6
1	1	2	25.7	30.5
1	1	0	97.5	86.7
1	1	1	83.3	103.7
1	2	11	29.7	-30.5
1	2	10	40.0	79.8
1	2	9	19.2	-14.0
1	2	8	27.1	-21.7
1	2	7	13.8	14.7
1	2	6	1210	20.6
1	2	5	1212	46.3
1	2	4	1213	10.0
1	2	3	1214	18.5
1	2	2	17.2	-23.5
1	2	1	44.0	43.9
1	2	0	20.8	19.9
1	3	12	67.8	-67.3
1	3	11	30.1	-37.2
1	3	10	42.6	61.0
1	3	8	31.4	29.6
1	3	7	93.7	-29.1
1	3	6	13.0	-7.9
1	3	4	12.7	-13.2
1	3	3	25.4	28.8
1	3	2	37.2	37.2
1	3	1	12.6	-12.6
1	4	12	12.1	-13.7
1	4	11	13.4	9.1
1	4	10	29.7	31.5
1	4	9	18.8	20.8
1	4	8	22.4	-19.9
1	4	7	23.7	25.2
1	4	6	30.9	32.0
1	4	5	25.1	-27.9
1	4	4	96.2	-43.2
1	4	3	62.2	51.7
1	4	2	25.1	-27.9
1	4	1	17.0	-19.8
1	4	0	13.0	-17.6
1	5	11	23.2	22.7
1	5	10	21.9	-23.7
1	5	9	23.2	-17.6
1	5	8	13.0	-17.6
1	5	7	50.1	47.4
1	5	6	43.3	-40.0
1	5	5	83.5	-79.6
1	5	4	34.1	29.7
1	5	3	11.1	12.4
1	5	2	52.7	45.8
1	5	1	81.1	77.4
1	6	11	100.1	-109.3
1	6	10	91.7	-102.8
1	6	8	94.7	100.2
1	6	4	54.2	42.4
1	6	3	20.7	-23.8
1	6	2	18.3	-13.9
1	6	1	13.4	-11.5
1	6	0	13.8	18.9
1	7	12	13.8	-18.9
1	7	11	17.8	8.4
1	7	10	42.4	-33.1
1	7	9	33.9	36.1
1	7	8	8.6	12.6
1	7	7	59.1	-56.4
1	7	5	94.8	94.1
1	7	3	18.2	-23.9
1	7	2	10.8	-14.1
1	8	1	18.0	22.1
1	8	-1	25.4	21.3
1	8	-5	73.3	69.2
1	8	-7	75.4	-66.7
1	8	-8	8.4	-10.8
1	8	-9	17.2	17.8
1	8	-11	14.4	-22.0
1	9	11	17.2	1.9
1	9	6	14.8	-16.9
1	9	5	46.0	-47.4
1	9	4	22.3	22.8
1	9	3	23.2	37.2
1	9	2	14.2	7.7
1	9	0	13.9	-8.7
1	9	-1	39.4	37.8
1	9	-2	34.9	-36.1
1	9	-3	72.5	-79.9
1	9	-4	36.4	31.5
1	9	-5	42.2	47.3
1	9	-6	15.9	-14.1
1	9	-7	16.6	-19.7
1	9	-11	12.6	9.8
1	9	-13	7.3	-10.2
1	10	10	14.9	-16.8
1	10	8	23.3	23.7
1	10	6	17.3	-20.0
1	10	5	26.2	-29.9
1	10	4	13.1	17.2
1	10	3	30.6	27.8
1	10	2	12.3	-14.4
1	10	-1	12.9	-9.4
1	10	-4	19.8	-22.9
1	10	-6	25.6	31.9
1	10	-7	13.5	13.9
1	10	-8	15.0	-13.5
1	10	-10	10.0	12.0
1	11	10	10.5	-12.8
1	11	4	10.5	-12.8
1	11	2	21.0	25.2
1	11	0	44.1	-38.8
1	11	-2	71.5	73.9
1	11	-6	10.5	-13.1
1	12	10	17.9	19.0
1	12	8	17.8	-21.9
1	12	6	8.4	10.8
1	12	5	17.1	-18.9
1	12	4	10.6	-14.7
1	12	-5	19.2	-22.0
1	12	-6	13.1	14.6
1	12	-10	12.4	-12.6
1	13	9	21.1	22.4
1	13	3	26.5	-29.4
1	13	-1	24.2	-17.9
1	13	-2	17.2	-14.0
1	13	-3	42.7	51.3
1	13	-4	17.3	15.6
1	13	-5	19.2	-18.7
1	14	9	31.1	-26.9
1	14	5	23.9	27.5
1	14	3	18.7	-20.8
1	14	-9	29.2	30.7
1	14	-7	23.7	-28.5
1	14	-9	12.8	13.0
1	15	5	12.1	-14.1
1	15	2	12.7	16.3
1	15	1	25.2	-28.4
1	15	0	29.8	25.5
1	15	-1	45.8	39.8
1	15	-2	25.5	-32.0
1	15	-3	29.2	-30.0
1	15	-4	24.7	17.3
1	15	-5	18.6	14.7
1	16	7	18.8	5.2
1	16	4	10.3	15.2
1	16	3	11.1	12.4
1	16	2	12.6	-13.0
1	16	-4	14.6	-19.7
1	16	-6	3.1	-0.0
2	0	13	3.1	-0.0
2	0	6	12.8	-9.9
2	0	4	76.4	-72.3
2	0	2	169.8	135.8
2	0	-4	41.8	49.2
2	0	-6	24.9	21.9
2	0	-12	59.2	57.8
2	0	-14	49.1	-39.9
2	0	-16	14.9	14.0
2	1	9	8.4	-8.1
2	1	8	41.5	-35.2
2	1	7	35.0	35.4
2	1	6	44.8	39.1
2	1	5	29.7	-24.0
2	1	4	42.4	-33.1
2	1	3	37.6	35.1
2	1	2	68.2	69.7
2	1	1	17.6	15.6
2	1	0	22.9	-21.2
2	1	-2	72.9	-84.0
2	1	-3	22.9	40.7
2	1	-4	38.1	37.7
2	1	-5	26.6	-27.9
2	1	-6	68.9	-63.1
2	1	-7	57.4	57.7
2	1	-8	70.7	78.6
2	1	-9	24.4	-26.5
2	1	-10	43.3	-49.2
2	1	-11	35.4	34.9
2	1	-12	32.6	23.4
2	1	-13	36.4	-34.9
2	2	7	12.8	9.2
2	2	6	29.7	-24.0
2	2	5	27.5	27.7
2	2	4	40.4	35.5
2	2	3	56.2	-52.0
2	2	2	7.7	4.3
2	2	1	43.0	-46.7
2	2	0	49.9	-39.0
2	2	-1	84.6	86.3
2	2	-3	11.5	-4.0
2	2	-5	55.1	-55.4
2	2	-6	21.9	-10.0
2	2	-7	9.7	-4.1
2	2	-8	6.4	-4.0
2	2	-9	18.6	22.0
2	2	-11	13.4	-14.9
2	2	-13	14.4	14.4
2	2	-15	13.4	-14.9
2	3	9	18.6	20.9
2	3	8	16.9	-13.5
2	3	7	56.2	-49.0
2	3	5	55.7	40.1
2	3	3	79.3	-58.6
2	3	2	11.5	14.0
2	3	0	8.1	-8.4
2	3	-3	74.8	-86.4
2	3	-4	18.1	14.2
2	3	-5	71.2	72.5
2	3	-7	69.5	-86.0
2	3	-8	26.5	17.9
2	3	-9	79.4	79.6
2	3	-11	32.9	-25.7
2	3	-13	21.1	17.9
2	4	7	18.5	-16.0
2	4	4	37.8	32.0
2	4	3	47.7	43.5
2	4	2	43.2	-39.2
2	4	1	17.8	-24.0
2	4	0	7.2	12.3
2	4	-1	18.5	7.2
2	4	-3	15.5	-15.9
2	4	-5	30.8	-17.9
2	4	-6	8.8	7.4
2	4	-7	13.8	11.1
2	4	-8	17.2	17.5
2	4	-11	14.4	12.4
2	4	12	13.3	-10.2
2	4	13	12.9	-10.3
2	4	14	7.5	8.3
2	4	15	10.0	12.9
2	4	16	29.8	27.1
2	5	8	13.2	13.8
2	5	6	30.9	-26.0
2	5	4	42.1	34.2
2	5	3	7.8	10.2
2	5	-2	23.7	-21.1
2	5	-4	8.3	-7.8
2	5	-6	32.4	-33.8
2	5	-8	9.5	-7.6
2	5	-10	18.5	-18.3
2	5	-13	12.7	-14.2
2	6	7	10.3	-12.0
2	6	4	50.4	-49.5
2	6	2	78.8	73.5
2	6	1	11.7	-13.0
2	6	0	79.6	-66.3
2	6	-1	34.8	28.9
2	6	-2	47.8	47.6
2	6	-3	10.7	-11.0
2	6	-4	50.6	-84.4
2	6	-5	9.4	12.4
2	6	-6	12.7	15.5
2	6	-7	6.8	8.6
2	6	-10	8.2	-4.4
2	6	-12	16.9	17.1
2	6	-14	22.1	22.7
2	6	-16	9.6	-9.2
2	7	9	7.7	-10.7
2	7	8	21.1	-27.2
2	7	7	25.8	31.7
2	7	6	23.8	22.7
2	7	5	24.6	-27.9
2	7	4	21.6	-24.3
2	7	3	28.5	32.2
2	7	2	36.4	40.1
2	7	1	17.9	-24.6
2	7	-1	32.0	-29.2
2	7	-2	38.5	-37.9
2	7	-3	53.5	51.9
2	7	-4	37.1	37.2
2	7	-5	30.9	-34.2
2	7	-6	47.1	-44.7
2	7	-7	50.2	50.2
2	7	-8	53.3	50.4
2	7	-9	46.0	-39.5
2	7	-10	32.4	-30.1
2	7	-11	34.3	35.0
2	7	-12	20.9	23.0
2	7	-13	19.3	-19.2
2	8	7	10.3	8.1
2	8	6	9.4	-11.8
2	8	5	23.3	26.2
2	8	3	47.8	-44.0
2	8	1	43.2	38.0
2	8	-1	29.1	-23.0
2	8	-3	18.3	18.0
2	8	-5	54.4	-44.2
2	8	-7	9.3	-14.0
2	8	-11	10.2	-7.2
2	9	13	23.7	-21.1
2	9	11	19.3	21.8
2	9	9	32.0	18.1
2	9	8	15.5	-19.2
2	9	7	38.9	-43.3
2	9	6	18.9	18.8
2	9	5	41.5	46.6
2	9	4	10.0	-9.6
2	9	-7	114.7	-87.3
2	9	-5	35.9	34.8
2	9	-9	51.2	49.1
2	9	-10	13.3	-10.4
2	9	-11	23.1	-22.9
2	10	7	15.9	-24.1
2	10	6	8.3	-11.0
2	10	4	21.4	26.0
2	10	3	19.2	22.9
2	10	2	22.6	-29.3
2	10	1	13.5	-16.7
2	10	0	18.6	22.9
2	10	-1	9.2	10.7
2	10	-2	16.7	-19.4
2	10	-3	19.0	-10.8
2	10	-4	33.3	25.8
2	10	-6	22.7	-17.2
2	10	-7	16.5	17.3
2	10	-12	11.3	-10.3
2	11	2	13.1	-13.6
2	11	-2	17.7	19.8
2	11	-4	18.0	-14.4
2	11	-6	18.6	-20.2
2	11	-10	20.3	23.0
2	11	12	14.5	-16.8
2	12	7	14.3	-16.0
2	12	4	16.4	-18.1
2	12	3	14.6	18.9
2	12	2	21.5	23.2
2	12	1	14.5	-18.1
2	12	0	11.8	-13.2
2	12	-2	18.5	20.8
2	12	-3	23.9	-17.0
2	12	-4	18.7	-19.5
2	12	-10	9.6	10.0
2	13	7	12.2	23.8
2	13	5	16.9	-27.7
2	13	3	16.3	17.4
2	13	-3	23.9	24.0
2	13	-4	21.8	19.7
2	13	-5	41.7	-40.8
2	13	-6	23.6	-25.4
2	13	-7	46.7	43.3
2	13	-8	22.6	23.7
2	13	-9	32.5	-35.1
2	13	-10	9.6	-9.8
2	14	3	17.4	-24.2
2	14	1	14.2	18.9
2	14	-3	16.7	16.7
2	14	-5	20.9	-15.6
2	14	-8	15.4	15.4
2	15	6	14.8	-15.4
2	15	5	16.7	12.2
2	15	4	30.6	-22.9
2	16	0	26.5	26.5
2	16	-2	18.6	-17.9
2	16	-4	21.9	23.1
2	16	-6	12.3	-12.1
3	0	10	11.2	-14.9
3	0	6	23.7	-21.6
3	0	4	33.3	26.9
3	0	2	62.4	-61.0
3	0	0	10.9	9.0
3	0	-6	79.6	89.4
3	0	-8	96.2	-82.6
3	0	-10	79.6	68.2
3	0	-12	78.3	-72.3
3	0	-14	34.2	34.6
3	1	10	7.9	-14.9
3	1	8	9.8	-12.9
3	1	6	23.7	17.2
3	1	4	14.8	-8.0
3	1	3	57.9	44.9
3	1	2	88.8	82.1
3	1	1	112.5	-103.6
3	1	0	104.5	-105.0
3	1	-1	34.2	38.9
3	1	-2	98.7	86.1
3	1	-4	36.9	-73.7
3	1	-6	27.0	33.4
3	1	-8	32.6	32.2
3	1	-9	6.7	19.5
3	1	-10	10.8	11.9
3	2	7	17.3	19.5
3	2	4	19.5	16.8
3	2	3	28.9	26.0
3	2	2	44.5	-39.3
3	2	1	14.7	-11.7
3	2	0	19.9	-15.8
3	2	-1	24.3	-28.9
3	2	-2	14.6	14.3
3	2	-3	14.2	-12.4
3	2	-4	14.7	-11.7

H	K	L	F OBS	F CALC
3	2	3	23.7	20.2
3	2	0	9.1	-10.7
3	2	-1	27.8	-25.6
3	2	-2	20.4	-19.7
3	2	-3	25.0	9.4
3	2	-4	21.3	25.4
3	2	-5	72.7	-100.6
3	2	-6	53.7	-59.4
3	2	-7	109.0	126.1
3	2	-8	42.4	39.8
3	2	-9	55.1	-47.4
3	2	-10	21.3	-19.0
3	2	-11	23.9	19.0
3	2	-13	25.4	-26.1
3	2	-15	10.7	12.4
3	3	7	24.5	-20.4
3	3	6	24.0	19.4
3	3	5	60.6	-52.9
3	3	2	11.3	10.2
3	3	1	93.2	87.1
3	3	-1	38.7	-39.7
3	3	-2	15.6	14.1
3	3	-3	64.9	95.1
3	3	-4	22.7	-20.3
3	3	-5	40.1	-44.6
3	3	-6	22.4	14.9
3	3	-7	25.1	20.4
3	3	-8	9.4	-5.4
3	3	-9	30.9	20.9
3	3	-10	12.1	-14.3
3	4	5	16.4	18.4
3	4	4	10.9	-11.2
3	4	3	14.1	-13.5
3	4	2	12.5	11.0
3	4	-2	11.5	-14.1
3	4	-3	14.7	-16.7
3	4	-4	12.0	13.9
3	4	-5	20.0	24.3
3	4	-6	19.5	-21.6
3	4	-7	24.2	-28.4
3	4	-8	24.6	26.8
3	4	-9	31.9	35.1
3	4	-10	22.2	-22.2
3	4	-11	24.5	-19.4
3	4	-12	19.9	13.2
3	4	-13	25.2	24.6
3	4	-14	23.0	-22.3
3	5	5	13.6	-11.7
3	5	3	14.7	14.8
3	5	2	78.0	-76.6
3	5	1	35.0	-29.3
3	5	0	46.5	48.2
3	5	-1	8.0	11.5
3	5	-2	44.6	-48.7
3	5	-3	20.6	-16.4
3	5	-4	36.1	35.2
3	5	-5	9.0	8.7
3	5	-7	9.1	-8.6
3	5	-10	32.2	26.0
3	5	-14	12.8	13.5
3	6	6	17.3	-19.5
3	6	5	17.0	19.0
3	6	4	23.0	27.4
3	6	3	12.5	-11.6
3	6	2	27.4	-28.6
3	6	1	18.9	22.0
3	6	-2	39.2	39.4
3	6	-4	41.5	-46.4
3	6	-5	17.4	20.7
3	6	-6	89.3	86.0
3	6	-7	27.3	-24.0
3	6	-8	50.4	-47.2
3	6	-9	9.0	7.0
3	6	-10	41.0	44.6
3	6	-12	38.0	-41.9
3	6	-14	25.1	29.3
3	7	5	40.4	37.0
3	7	4	14.7	15.0
3	7	-1	39.7	43.4
3	7	-4	12.6	14.4
3	7	-6	19.4	18.0
3	7	-8	12.2	10.9
3	7	-12	14.0	14.6
3	7	-13	14.6	-15.0
3	7	-14	14.7	-19.7
3	7	-15	12.3	13.7
3	8	7	18.5	21.0
3	8	5	29.6	-30.1
3	8	3	19.1	18.6
3	8	1	12.9	-19.2
3	8	0	13.3	-14.0
3	8	-1	19.9	-27.1
3	8	-3	19.4	13.6
3	8	-4	19.6	16.7
3	8	-5	19.8	14.0
3	8	-9	41.6	-37.6
3	8	-10	12.2	-11.0
3	8	-11	33.8	32.8
3	8	-13	18.1	-23.2
3	9	5	14.0	13.1
3	9	3	24.1	-31.5
3	9	2	19.6	21.5
3	9	1	32.7	43.0
3	9	0	14.2	-14.7
3	9	-1	21.6	-27.9
3	9	-2	10.5	11.6
3	9	-3	45.6	44.3
3	9	-4	37.1	-35.7
3	9	-5	52.4	-59.4
3	9	-6	23.1	24.4
3	10	5	19.4	22.5
3	10	2	12.1	12.9
3	10	-2	18.3	-19.4
3	10	-3	18.3	-18.6
3	10	-4	29.3	20.9
3	10	-5	28.7	20.9
3	10	-6	36.6	-38.4
3	10	-7	30.0	-24.4
3	10	-8	34.3	28.2
3	10	-9	20.2	18.3
3	10,10		15.6	-15.9
3	10,11		15.1	-18.4
3	10,12		14.3	18.1
3	10,13		12.4	12.6
3	11	2	50.4	-47.0
3	11	0	9.4	5.6
3	11	-2	58.6	-40.2
3	11	-6	12.1	10.3
3	11,10		13.6	13.2
3	12	3	11.8	-14.4
3	12	-4	25.3	-17.9
3	12	-5	12.2	8.4
3	12	-6	17.3	17.2
3	12	-7	14.1	-10.6
3	12	-8	27.6	-26.0
3	12	-9	11.7	10.1
3	12,10		25.7	22.8
3	12,12		14.7	-14.5
3	12,13		10.2	13.0
3	13	3	15.9	20.3
3	13	1	30.1	-24.6
3	13	0	12.1	-9.5
3	13	-1	22.2	15.3
3	13	-2	14.1	11.3
3	13	-3	35.2	-31.3
3	13	-4	14.1	-15.4
3	13	-5	35.6	29.0
3	13	-6	12.1	10.4
3	13	-7	11.9	-11.8
3	13	-9	12.7	-11.1
3	14	1	14.5	13.5
3	14	-3	15.4	13.0
3	14	-5	29.6	-30.7
3	14	-7	39.4	37.5
3	15	2	15.9	19.0
3	15	1	33.1	34.7
3	15	0	20.9	-31.1
3	15	-2	27.1	22.6
3	15	-4	16.1	-15.7
3	15	-5	17.8	-14.4
3	16	-4	16.1	13.9
3	16	-5	17.7	10.6
3	16	-6	45.8	-33.6
4	0	6	20.3	-20.4
4	0	4	48.0	41.6
4	0	2	67.7	-54.3
4	0	-6	48.1	-41.7
4	0	-8	15.4	12.6
4	0	-12	66.0	-69.7
4	1	14	19.2	-12.9
4	1	7	27.5	-22.6
4	1	6	20.5	-18.5
4	1	5	11.2	12.1
4	1	4	12.3	9.4
4	1	3	26.2	-24.7
4	1	-1	27.1	28.9
4	1	-2	22.5	19.3
4	1	-3	26.2	-24.7
4	1	-4	21.4	-17.6
4	1	-5	5.4	7.6
4	1	-7	19.9	-27.1
4	1	-8	19.4	13.6
4	1	-9	19.6	11.7
4	1	-10	12.0	10.2
4	1	-11	19.6	13.0
4	1	-13	23.4	20.2
4	2	7	20.4	-17.4
4	2	6	41.2	-52.2
4	2	5	17.7	16.6
4	2	4	19.0	18.2
4	2	3	19.0	16.6
4	2	2	17.7	16.4
4	2	1	41.4	41.6
4	2	0	16.3	-12.8
4	2	-1	43.6	42.3
4	2	-2	27.3	27.8
4	2	-3	41.3	-49.8
4	2	-4	22.1	-21.2
4	2	-5	70.1	86.8
4	2	-6	31.9	39.6
4	2	-7	37.1	-44.6
4	2	-8	14.1	-13.3
4	2	-9	7.1	8.6
4	3	0	19.2	15.6
4	3	-1	27.1	42.3
4	3	-3	49.6	50.9
4	3	-4	21.4	-20.5
4	3	-5	24.8	-35.3
4	3	-7	28.4	34.1
4	3	-8	16.1	-11.3
4	3	-9	72.7	-82.2
4	4	5	18.4	15.8
4	4	4	31.7	-23.0
4	4	3	27.1	26.9
4	4	-1	28.4	30.9
4	4	-3	49.6	50.9
4	4	-4	21.4	-20.5
4	4	-5	27.1	-23.0
4	4	-6	11.1	14.8
4	4	-8	22.3	19.4
4	4	-9	30.5	27.3
4	4	-10	8.2	-7.0
4	4	-11	24.9	-20.1
4	4	-12	12.2	-4.2
4	4	-13	14.5	11.5
4	4	-15	11.5	-11.3
4	5	5	10.2	-17.3
4	5	4	11.0	15.0
4	5	0	17.4	-11.7
4	5	-2	15.1	-10.0
4	5	-4	39.4	39.8
4	5	-5	7.3	6.8
4	5	-6	35.2	26.5
4	5	-8	40.7	35.6
4	5	-9	7.9	9.6
4	5	-10	47.0	-36.8
4	6	8	13.6	-4.4
4	6	6	35.5	29.5
4	6	2	36.1	-34.9
4	6	0	82.8	86.3
4	6	-2	84.8	-88.9
4	6	-3	19.7	17.6
4	6	-4	71.1	74.5
4	6	-6	29.5	24.7
4	6	-8	8.7	7.9
4	6	-10	20.2	-21.5
4	6	-11	33.6	-32.9
4	6	-12	35.4	24.7
4	6	-14	30.1	24.7
4	7	5	12.0	-11.7
4	7	3	11.1	12.5
4	7	2	12.5	-16.2
4	7	-2	9.0	9.8
4	7	-3	52.0	-40.0
4	7	-4	27.6	-29.1
4	7	-5	11.1	12.5
4	7	-7	24.0	-23.7
4	7	-8	32.7	-32.3
4	7	-9	45.4	44.6
4	7	-10	27.0	31.2
4	7	-11	25.1	-31.7
4	7	-12	13.0	-13.7
4	8	7	22.4	-20.7
4	8	5	18.4	19.9
4	8	1	30.4	-31.9
4	8	-1	78.0	85.5
4	8	-2	17.7	16.6
4	8	-3	54.6	-47.2
4	8	-4	19.0	-19.9
4	8	-5	85.7	98.2
4	8	-6	9.8	13.0
4	8	-7	18.5	-16.2
4	8	-11	18.4	18.7
4	9	13	29.7	-25.6
4	9	7	18.8	20.9
4	9	5	21.6	-24.1
4	9	3	15.9	14.1
4	9	-3	35.3	29.5
4	9	-4	21.1	-18.3
4	9	-5	48.7	-47.1
4	9	-7	58.7	62.9
4	9	-8	37.9	-32.5
4	9	-9	53.1	-47.1
4	9-10		13.0	15.0
4	9-11		12.9	11.8
4	10	6	15.6	19.2
4	10	4	14.9	-18.0
4	10	3	11.0	-14.2
4	10	1	22.5	23.3
4	10	0	44.4	-32.6
4	10	-1	36.5	-29.2
4	10	-2	49.7	41.1
4	10	-3	27.8	22.7
4	10	-4	37.2	-30.6
4	10	-5	37.1	-43.0
4	10	-6	33.9	26.6
4	10	-8	23.3	-25.0
4	10-12		20.5	19.2
4	10-14		9.1	-11.2
4	11	-6	36.6	40.9
4	11-10		21.8	-19.5
4	12	2	10.6	-11.9
4	12	0	34.6	27.2
4	12	-1	26.3	-21.6
4	12	-2	46.4	-40.6
4	12	-3	18.4	14.0
4	12	-4	34.6	28.4
4	12	-6	22.5	-17.2
4	12-12		12.2	-10.5
4	13	-1	12.6	-4.9
4	13	-3	27.9	-17.7
4	13	-4	20.3	-12.4
4	13	-5	34.4	26.3
4	13	-7	35.3	-33.5
4	14	-1	19.9	-19.2
4	14	-4	12.2	-4.2
4	15	-5	11.1	-10.2
4	15	-6	10.8	10.1
4	15	-7	19.8	13.9
4	15	-8	17.1	-17.6
4	15	-9	16.3	-17.0
4	15-10		14.1	15.4
4	16	-4	31.8	-25.3
4	16	-6	22.8	20.0
4	16	-8	20.8	20.9
5	0	4	30.9	-29.6
5	0	2	33.0	27.0
5	0	-2	38.6	-34.3
5	0	-4	25.7	31.5
5	0	-6	37.2	-33.2
5	0	-8	12.4	12.6
5	0-10		71.6	-74.7
5	0-12		77.6	82.1
5	1	3	30.2	-27.1
5	1	2	33.1	-24.6
5	1	1	58.2	90.9
5	1	0	41.9	39.2
5	1	-1	10.5	-11.2
5	1	-2	46.9	-44.0
5	1	-3	7.3	8.6
5	1	-4	21.6	35.3
5	1	-5	8.7	-14.8
5	1	-6	10.5	-27.6
5	1-12		10.8	-26.7
5	1-13		21.7	15.1
5	1-14		30.6	31.0
5	1-15		24.7	-18.1
5	1-16		21.5	-21.4
5	2	5	30.0	30.4
5	2	4	14.5	11.4
5	2	3	24.8	-20.0
5	2	-1	10.9	8.9
5	2	-2	11.0	10.9
5	2	-3	8.1	-11.1
5	2	-4	20.5	-23.1
5	2	-5	51.0	72.6
5	2	-6	32.8	37.6
5	2	-7	55.9	-63.6
5	2	-8	14.6	-19.6
5	2	-9	23.1	25.2
5	2-10		12.5	11.7
5	2-11		29.1	-28.0
5	3	3	30.5	22.3
5	3	1	34.5	-29.1
5	3	-3	41.2	-41.0
5	3	-4	13.6	14.9
5	3	-5	23.4	22.7
5	3	-7	32.0	-35.7
5	3-15		29.9	29.7
5	4	5	20.8	-20.9
5	4	3	15.4	13.9
5	4	2	20.0	-20.5
5	4	-5	19.0	-16.8
5	4	-6	12.7	11.7
5	4	-8	12.6	-15.2
5	4-10		27.3	25.9
5	4-11		30.3	26.8
5	4-12		19.6	-15.5
5	5	2	33.9	31.4
5	5	1	16.8	14.4
5	5	0	17.7	-18.9
5	5	-2	19.5	19.0
5	5-12		23.6	21.0
5	5-14		30.8	29.6
5	6	4	24.4	-23.8
5	6	2	19.8	18.5
5	6	-2	21.0	-17.9
5	6	-4	44.7	38.5
5	6	-5	19.3	-12.5
5	6	-6	61.6	-53.8
5	6	-7	12.5	14.9
5	6	-8	27.4	29.5
5	6-10		51.3	-48.0
5	6-11		15.2	12.9
5	6-12		38.8	40.7
5	7	3	24.9	-25.5
5	7	2	21.8	-21.9
5	7	1	38.3	42.0
5	7	0	34.1	34.9
5	7	-1	32.6	-33.6
5	7	-2	31.6	-33.9
5	7	-3	27.6	26.6
5	7	-4	33.5	29.4
5	7	-5	25.8	-18.7
5	7	-6	18.5	-15.9
5	7-12		19.9	-19.1
5	7-13		25.9	27.3
5	7-14		25.6	26.4
5	7-15		22.7	-23.1
5	7-16		11.7	-13.4
5	8	5	22.9	25.3
5	8	3	19.2	-14.9
5	8	2	18.2	-14.9
5	8	-5	55.5	-47.9
5	8	-7	57.5	-50.2
5	8	-9	27.4	23.8
5	8-11		49.6	-40.1
5	9	3	18.5	15.4
5	9	1	15.4	14.6
5	9	-4	26.8	27.1
5	9	-5	45.5	43.4
5	9	-6	19.0	-15.4
5	9	-7	27.2	-23.2
5	9-13		17.9	-11.5
5	9-15		18.8	16.7
5	10	-4	35.1	-26.4
5	10	-6	31.7	28.3
5	10-10		21.6	20.6
5	10-11		17.1	14.9
5	10-12		19.2	-15.1
5	11	2	17.6	23.4
5	11	1	27.9	-0.3
5	11	-1	27.9	-11.6
5	11-12		13.1	9.6
5	11-14		19.9	-21.9
5	12	-4	21.9	19.2
5	12-10		25.4	-19.9
5	12	-5	18.7	19.1
5	13	-5	26.7	-22.2
5	13	-6	14.5	-11.7
5	13	-7	20.3	11.9
5	14	-5	28.1	25.1
5	14	-7	27.3	-22.9
6	0	4	20.6	-19.4
6	0	2	27.6	24.3
6	0	0	71.4	-73.6
6	0	-2	72.1	82.8
6	0	-4	27.5	-29.7
6	0	-8	12.5	15.1
6	0-10		19.6	-19.2
6	0-12		52.6	56.0
6	0-14		49.3	-41.8
6	0-16		27.7	27.0
6	1	3	14.9	13.2
6	1	2	19.5	16.0
6	1	1	17.0	19.4
6	1	0	22.7	-14.9
6	1	-1	23.3	-24.1
6	1	-2	9.3	9.5
6	1	-4	22.0	44.0
6	1	-5	19.4	-27.3
6	1	-6	21.5	-47.2
6	1	-7	24.1	30.9
6	1	-8	17.2	12.1
6	1	-9	29.6	-27.9
6	1	-10	20.0	21.7
6	1-11		33.6	37.9
6	1-12		40.9	39.7
6	1-13		37.8	-37.5
6	1-14		12.3	-12.1
6	2	3	20.9	-16.6
6	2	1	17.2	-12.5
6	2	-1	21.7	-15.9
6	2	-2	14.1	12.4
6	2	-3	20.9	-16.6
6	2	-4	17.2	-12.5
6	2	-5	43.0	49.6
6	3	-1	29.1	-26.1
6	3	-3	34.9	37.3
6	3	-4	43.0	49.6
6	3	-5	47.2	43.0
6	4	0	20.6	18.2
6	4	-1	27.4	-26.2
6	4	-3	30.5	-32.3
6	4	-5	16.6	-16.8
6	4	-6	36.8	34.9
6	4	-7	9.7	10.1
6	4	-8	28.9	-30.0
6	4	-10	11.2	11.7
6	4	-11	23.6	21.3
6	4	-12	27.9	-27.3
6	4	-13	19.1	-15.4
6	4	-14	20.7	22.8
6	4	-15	17.0	14.0
6	4	-16	20.3	-27.9
6	4	-17	18.8	22.1
6	5	4	20.8	22.1
6	5	3	14.9	14.8
6	5	2	18.2	21.9
6	5	-2	14.3	14.8
6	5	-4	18.0	20.0
6	5	-5	44.1	-39.9
6	5	-6	43.2	-40.1
6	5	-7	49.2	37.9
6	5	-8	35.6	31.9
6	5	-9	30.2	-29.7
6	5	-10	31.0	-29.2
6	5	-11	23.8	-24.9
6	5	-12	34.9	30.3
6	5	-13	36.8	33.4
6	5	-14	23.8	-24.9
6	5	-15	13.8	-11.9
6	6	4	11.9	12.7
6	6	-1	31.5	-30.3
6	6	-3	21.0	23.3
6	6	-5	26.4	-10.2
6	6	-9	15.0	15.6
6	6	-11	15.1	-16.7
6	6	-13	14.2	13.8
6	7	3	9.5	6.4
6	7	-1	53.8	53.8
6	7	-3	37.6	-33.2
6	7	-5	73.6	-71.3
6	7	-7	21.3	21.6
6	7	-9	42.8	37.0
6	7	-11	24.2	-20.9
6	7	-13	15.5	16.4
6	8	2	14.2	13.8
6	8	-2	10.2	14.2
6	8	-4	16.9	12.0
6	8	-6	19.2	-22.0
6	8	-10	14.1	14.4
6	8	-12	22.0	-26.0
6	9	-1	13.2	13.2
6	9	-3	14.9	13.2
6	9	-5	19.5	16.0
6	9	-7	17.0	19.4
6	9	-9	27.0	-27.3
6	9	-11	44.0	44.0
6	9	-13	20.8	22.1
6	10	-2	30.4	29.2
6	10	-4	14.6	14.2
6	10	-6	16.2	16.0
6	10	-8	19.5	19.2
6	10	-10	14.4	14.2
6	10	-12	14.1	14.4
6	11	-1	14.1	14.4
6	11	-3	14.2	14.2
6	11	-5	14.2	14.2
6	11	-7	14.2	14.2
6	11	-9	14.2	14.2
6	11	-11	14.2	14.2
6	12	-2	14.2	14.2
6	12	-4	14.2	14.2
6	12	-6	14.2	14.2
6	12	-8	14.2	14.2
6	12	-10	14.2	14.2
6	13	-1	14.2	14.2
6	13	-3	14.2	14.2
6	13	-5	14.2	14.2
6	13	-7	14.2	14.2
6	13	-9	14.2	14.2
6	13	-11	14.2	14.2
6	14	-2	14.2	14.2
6	14	-4	14.2	14.2
6	14	-6	14.2	14.2
6	14	-8	14.2	14.2
6	14	-10	14.2	14.2
6	14	-12	14.2	14.2
6	15	-1	14.2	14.2
6	15	-3	14.2	14.2
6	15	-5	14.2	14.2
6	15	-7	14.2	14.2
6	15	-9	14.2	14.2
6	15	-11	14.2	14.2
6	16	-2	14.2	14.2
6	16	-4	14.2	14.2
6	16	-6	14.2	14.2
6	16	-8	14.2	14.2
6	16	-10	14.2	14.2
6	16	-12	14.2	14.2
6	17	-1	14.2	14.2
6	17	-3	14.2	14.2
6	17	-5	14.2	14.2
6	17	-7	14.2	14.2
6	17	-9	14.2	14.2
6	17	-11	14.2	14.2
6	18	-2	14.2	14.2
6	18	-4	14.2	14.2
6	18	-6	14.2	14.2
6	18	-8	14.2	14.2
6	18	-10	14.2	14.2
6	18	-12	14.2	14.2
6	19	-1	14.2	14.2
6	19	-3	14.2	14.2
6	19	-5	14.2	14.2
6	19	-7	14.2	14.2
6	19	-9	14.2	14.2
6	19	-11	14.2	14.2
6	20	-2	14.2	14.2
6	20	-4	14.2	14.2
6	20	-6	14.2	14.2
6	20	-8	14.2	14.2
6	20	-10	14.2	14.2
6	20	-12	14.2	14.2
6	21	-1	14.2	14.2
6	21	-3	14.2	14.2
6	21	-5	14.2	14.2
6	21	-7	14.2	14.2
6	21	-9	14.2	14.2
6	21	-11	14.2	14.2
6	22	-2	14.2	14.2
6	22	-4	14.2	14.2
6	22	-6	14.2	14.2
6	22	-8	14.2	14.2
6	22	-10	14.2	14.2

TABLE 27

$Cu(\alpha\text{-pic})_2(NO_3)_2$ - Form II

Observed and final-calculated structure amplitudes

H	K	L	F OBS	F CALC
0	0	8	18.5	22.2
0	0	6	52.1	-58.6
0	0	4	49.1	-42.5
0	0	2	65.0	-63.5
0	1	14	30.9	-27.6
0	1	13	10.3	10.5
0	1	12	36.5	30.8
0	1	11	30.1	-26.2
0	1	8	32.2	33.2
0	1	7	43.5	-46.8
0	1	6	33.3	-30.0
0	1	5	12.3	-10.6
0	1	4	18.6	-13.9
0	1	3	40.2	38.4
0	1	2	27.7	-27.9
0	2	9	10.2	-10.3
0	2	7	58.7	57.3
0	2	6	40.4	42.6
0	2	5	21.1	-24.2
0	2	3	72.2	-51.4
0	2	2	100.9	104.3
0	2	1	804.9	1104.2
0	3	14	10.1	13.3
0	3	13	26.9	-24.5
0	3	11	34.0	29.0
0	3	7	53.4	52.2
0	3	6	8.0	6.8
0	3	5	70.7	-64.2
0	3	4	19.4	17.4
0	3	3	12.9	-7.6
0	3	2	40.1	39.6
0	3	1	53.1	-42.8
0	4	7	37.8	-35.4
0	4	6	39.3	35.1
0	4	5	82.1	73.9
0	4	4	36.5	-31.8
0	4	3	78.0	-76.7
0	4	1	69.4	76.3
0	5	14	8.0	10.1
0	5	13	29.1	24.4
0	5	9	23.1	20.6
0	5	7	22.4	-21.9
0	5	6	59.9	52.1
0	5	5	26.2	21.4
0	5	4	49.1	-42.5
0	5	3	30.7	-27.3
0	6	2	26.6	27.2
0	6	A	17.0	15.2
0	6	6	54.3	-49.5
0	6	5	40.4	-37.2
0	6	4	69.1	64.8
0	6	3	17.8	23.3
0	6	2	108.7	1118.0
0	6	C	73.5	67.8
0	7	12	20.6	20.1
0	7	10	11.1	-12.5
0	7	9	18.1	16.8
0	7	8	35.6	30.7
0	7	6	32.5	-30.6
0	7	4	23.7	21.3
0	7	3	19.4	20.8
0	7	2	20.2	-21.8
0	8	12	7.6	8.1
0	8	8	47.6	43.0
0	8	4	37.9	-35.4
0	8	J	22.2	22.4
0	8	2	46.7	45.7
0	8	1	47.6	-45.7
0	9	0	82.5	-74.8
0	9	13	20.4	-21.4
0	9	12	13.2	-14.3
0	9	11	9.8	10.6
0	9	9	23.9	-22.6
0	9	7	16.9	17.8
0	9	6	20.2	20.0
0	9	5	13.2	-14.6
0	9	4	17.9	-19.4
0	9	3	34.2	33.4
0	9	2	7.5	8.6
0	9	1	25.6	22.5
0	10	7	32.1	-31.5
0	10	5	24.7	24.6
0	10	3	43.9	-41.3
0	10	2	18.1	14.8
0	10	1	81.4	80.6
0	11	9	23.8	25.1
0	11	7	12.6	-12.7
0	12	8	12.8	13.9
0	12	6	20.2	20.0
0	12	4	11.2	-15.2
0	12	2	27.1	27.9
0	13	1	11.8	11.2
0	14	2	11.0	12.1
0	14	0	22.2	22.7
0	15	1	25.7	-25.8
0	16	0	9.9	14.7
0	16	1	12.3	-15.8
0	16	3	10.8	15.0
0	16	2	30.2	30.2
0	16	0	51.2	-53.5
0	16	3	17.2	-19.0
0	16	1	32.1	30.1
1	0	12	20.5	21.2
1	0	10	37.4	-32.7
1	0	8	46.0	48.2
1	0	6	9.8	-14.5
1	0	4	92.6	-49.6
1	1	10	17.0	16.1
1	1	8	36.1	-37.0
1	1	7	33.3	32.8
1	1	6	37.7	46.4
1	1	5	12.5	-17.1
1	1	4	7.9	17.9
1	1	2	16.7	-12.3
1	1	1	52.2	-59.4
1	2	11	25.2	23.7
1	2	10	22.2	17.4
1	2	9	19.8	-20.4
1	2	8	21.3	-20.1
1	2	7	56.4	54.5
1	2	6	20.6	21.6
1	2	5	15.6	-17.9
1	2	4	11.4	-15.2
1	2	3	21.1	20.0
1	2	2	18.0	15.0
1	2	1	107.3	94.6
1	3	6	36.6	-38.6
1	3	5	89.1	-80.5
1	3	4	43.2	37.7
1	3	3	9.5	9.1
1	3	2	10.8	8.4
1	3	1	67.6	79.8
1	3	0	91.3	-100.0
1	4	7	72.7	71.2
1	4	6	50.7	-55.6
1	4	5	99.4	98.4
1	4	4	19.3	23.6
1	4	3	82.7	-76.8
1	4	2	35.8	-29.1
1	4	1	55.6	53.8
1	4	0	8.9	8.3
1	5	9	19.3	-15.6
1	5	8	31.7	-26.4
1	5	7	23.0	-20.6
1	5	6	31.7	-35.6
1	5	5	35.2	25.4
1	5	4	19.3	23.6
1	5	3	43.9	-37.1
1	5	2	45.4	37.1
1	5	1	62.3	55.1
1	5	0	32.7	29.6
1	6	8	55.8	-49.0
1	6	A	9.1	10.2
1	6	9	46.5	43.3
1	6	10	12.2	-12.8
1	6	11	10.5	12.2
1	6	12	11.0	-13.6
1	7	9	11.1	-11.9
1	7	8	10.7	11.2
1	7	7	27.6	25.0
1	7	6	23.9	-25.3
1	7	5	24.3	23.9
1	7	4	56.4	-58.0
1	7	3	52.4	46.8
1	7	1	120.7	109.8
1	7	0	102.1	-83.6
1	8	12	22.1	19.3
1	8	10	15.4	-14.0
1	8	9	21.3	20.1
1	8	8	30.3	26.6
1	8	7	17.1	12.5
1	8	6	28.0	-24.8
1	8	5	36.6	37.6
1	8	4	10.0	-11.0
1	8	3	18.0	20.4
1	8	2	8.7	8.3
1	8	1	9.3	10.4
1	8	0	13.0	-12.0
1	9	12	25.0	19.6
1	9	11	42.9	29.9
1	9	5	38.3	30.3
1	9	4	72.2	63.8
1	9	3	41.0	36.5
1	9	2	44.6	59.6
1	9	1	21.3	22.7
1	10	9	21.2	-23.0
1	10	8	25.4	-24.7
1	10	7	22.4	20.2
1	10	6	19.9	-15.0
1	10	5	14.5	16.3
1	10	4	22.4	24.0
1	10	3	18.5	-19.2
1	10	2	24.6	-22.1
1	10	1	57.4	-43.8
1	10	0	83.9	70.7
1	11	9	19.6	17.2
1	11	8	14.2	13.2
1	11	7	20.1	-19.1
1	11	6	39.7	39.2
1	11	5	13.9	-16.4
1	11	4	39.4	39.7
1	11	3	12.8	15.4
1	11	2	66.1	-62.2
1	11	1	67.2	77.3
1	11	A	159.4	155.9
1	11	9	18.9	-18.3
1	11	10	29.9	-32.9
1	11	12	20.1	19.9
1	12	8	20.2	19.4
1	12	7	38.5	-40.5
1	12	6	55.5	-57.9
1	12	5	64.2	71.9
1	12	4	41.9	52.6
1	12	3	39.3	-40.1
1	12	2	22.8	-25.1
1	12	1	72.3	74.3
1	12	0	16.3	-10.2
1	13	1	191.2	1181.3
1	13	3	47.2	-29.4
1	13	4	12.5	-6.8
1	13	5	29.9	-27.5
1	13	6	59.3	-55.7
1	13	7	92.9	80.2
1	13	8	37.0	33.6
1	13	9	23.8	-20.9
1	13	11	22.9	-20.3
1	13	13	73.8	70.0
1	13	15	36.3	-26.6
1	14	0	15.7	15.5
1	14	1	90.4	79.4
1	14	2	7.6	8.4
1	14	3	125.4	1106.0
1	14	5	19.5	-19.5
1	14	7	30.2	29.5
1	14	9	27.5	29.0
1	14	11	22.8	-17.6
1	14	13	29.0	29.2
1	14	14	12.4	11.0
1	15	0	20.5	25.0
1	15	1	48.2	54.4
1	15	2	36.7	30.4
1	15	3	65.6	54.3
1	15	4	30.7	230.2
1	15	5	51.1	-47.0
1	15	6	24.3	18.1
1	15	7	23.7	18.8
1	15	9	19.8	-15.7
1	15	11	20.4	19.3
1	15	13	22.3	-17.8
1	15	15	33.6	-30.6
2	0	8	24.6	-22.1
2	0	4	56.1	-62.8
2	0	2	57.4	-43.8
2	0	24	83.9	70.7
2	0	6	85.1	67.6
2	0	8	66.2	-69.2
2	1	11	19.6	17.2
2	1	10	14.2	13.2
2	1	8	20.1	-19.1
2	1	7	17.8	20.6
2	1	6	36.4	39.7
2	1	4	15.4	-17.7
2	1	1	12.8	15.4
2	1	6	86.1	-62.2
2	1	7	87.2	77.3
2	1	8	159.4	155.9
2	1	9	18.9	-18.3
2	1	10	29.9	-32.9
2	1	12	20.1	19.9
2	2	8	20.2	19.4
2	2	7	38.5	-40.5
2	2	6	55.5	-57.9
2	2	5	64.2	71.9
2	2	4	41.9	52.6
2	2	3	39.3	-40.1
2	2	2	22.8	-25.1
2	2	1	72.3	74.3
2	2	0	16.3	-10.2
2	2	1	191.2	1181.3
2	2	3	47.2	-29.4
2	2	4	12.5	-6.8
2	2	5	29.9	-27.5
2	2	6	59.3	-55.7
2	2	7	92.9	80.2
2	2	8	37.0	33.6
2	2	9	23.8	-20.9
2	2	11	22.9	-20.3
2	3	0	12.4	12.8
2	3	1	26.7	-24.3
2	3	2	73.8	70.0
2	3	3	36.3	-26.6
2	3	4	15.7	15.5
2	3	5	90.4	79.4
2	3	6	7.6	8.4
2	3	7	125.4	1106.0
2	3	8	19.5	-19.5
2	3	9	30.2	29.5
2	3	10	27.5	29.0
2	3	11	22.8	-17.6
2	3	13	29.0	29.2
2	4	11	12.4	11.0
2	4	9	27.0	223.9
2	4	7	40.7	40.1
2	4	6	21.9	-16.8
2	4	5	68.4	276.7
2	4	4	13.8	13.8
2	4	3	53.1	61.0
2	4	2	25.2	21.9
2	4	1	35.3	-35.7
2	4	0	20.5	25.0
2	4	1	48.2	54.4
2	4	2	36.7	30.4
2	4	3	65.6	54.3
2	4	4	30.7	230.2
2	4	5	51.1	-47.0
2	4	6	24.3	18.1
2	4	7	23.7	18.8
2	4	9	19.8	-15.7
2	4	11	20.4	19.3
2	4	13	22.3	-17.8
2	4	15	33.6	-30.6
2	5	0	22.3	-17.8
2	5	1	9.3	8.6
2	5	2	28.4	29.4
2	5	3	24.5	-31.0
2	5	5	10.4	-9.4
2	5	6	85.9	75.6
2	5	7	51.0	35.3
2	5	8	24.7	6.2
2	5	9	24.2	-21.9
2	5	9	65.5	-56.1
2	5	10	22.4	19.1
2	5	11	17.4	13.4
2	5	12	26.2	-20.7
2	5	13	37.9	-31.8
2	5	15	24.7	6.2
2	6	10	18.4	15.5
2	6	8	28.1	-26.8
2	6	7	21.6	-19.4
2	6	6	34.0	36.5
2	6	5	14.7	13.3
2	6	4	29.0	-22.2
2	6	3	11.5	11.0
2	6	2	34.6	42.1
2	6	1	8.8	11.8
2	6	0	14.9	-16.2
2	6	1	29.1	-35.7
2	6	3	29.1	25.6
2	6	4	59.7	-54.3
2	6	5	25.9	-18.6
2	6	6	36.9	36.2
2	6	8	19.5	-16.6
2	7	10	22.4	20.2
2	7	8	36.7	-36.2
2	7	6	18.9	18.8
2	7	4	11.4	11.3
2	7	0	26.4	23.1
2	7	1	29.8	-28.6
2	7	2	43.3	-39.4
2	7	3	22.4	-16.4
2	7	24	39.6	33.4
2	7	6	38.0	-33.9
2	7	8	67.0	67.9
2	7	10	38.3	37.4
2	7	12	32.2	25.6
2	8	8	32.3	30.6
2	8	7	19.2	-18.7
2	8	6	42.1	-39.9
2	8	5	19.9	20.7
2	8	4	29.5	35.1
2	8	3	29.5	-25.7
2	8	2	18.6	19.4
2	8	1	67.3	65.1
2	8	0	50.5	49.2
2	8	-1	58.3	54.6
2	8	-2	78.7	60.1
2	8	-3	45.1	38.0
2	8	-4	29.3	24.5
2	8	-5	10.3	11.3
2	8	-6	49.9	38.4
2	8	-8	40.7	38.5
2	8	-9	18.7	14.4
2	9	10	9.2	10.2
2	9	9	15.2	15.6
2	9	7	20.2	20.0
2	9	5	12.5	11.7
2	9	4	14.1	14.3
2	9	3	23.6	21.2
2	9	1	25.5	26.5
2	9	-2	21.9	18.3
2	9	-3	39.1	33.8
2	9	-4	35.2	29.6
2	9	-5	24.7	19.9
2	9	-6	34.2	30.2
2	9	-7	53.2	41.9
2	9	-8	20.7	19.2
2	9	-9	56.7	48.2
2	9	-11	12.4	14.7
2	10	7	45.3	43.3
2	10	5	44.2	43.3
2	10	3	33.2	32.5
2	10	1	39.5	35.6
2	10	0	13.3	12.8
2	10	-1	53.7	42.6
2	10	-3	39.3	31.2
2	10	-5	31.0	25.3
2	10	-6	29.4	24.4
2	10	-7	45.4	38.1
2	10	-9	26.2	26.6
2	11	7	11.3	12.9
2	11	5	21.5	21.1
2	11	4	17.8	17.5
2	11	-2	12.0	13.0
2	11	-4	38.3	33.4
2	11	-5	44.2	34.4
2	11	-6	20.3	18.7
2	11	-9	36.6	35.0
2	11	10	12.0	12.6
2	11	11	25.3	22.2
2	12	7	12.0	12.6
2	12	6	19.6	19.5
2	12	5	28.4	27.9
2	12	4	25.7	20.6
2	12	3	17.7	17.9
2	12	2	31.7	29.8
2	12	1	16.2	14.5
2	12	0	20.4	17.2
2	12	-1	16.1	13.7
2	12	-2	43.7	37.3
2	12	-4	27.0	21.5
2	12	-5	12.5	11.3
2	12	-7	32.3	27.6
2	12	-8	20.1	17.1
2	13	6	10.3	11.2
2	13	4	15.1	16.3
2	13	1	12.5	14.9
2	13	-1	21.7	20.6
2	13	-3	12.5	14.2
2	13	-6	45.7	41.3
2	13	-7	32.9	29.4
2	13	-8	23.5	20.3
2	13	-9	32.8	27.9
2	13	10	19.7	17.9
2	14	6	22.9	22.8
2	14	4	31.6	29.9
2	14	2	33.2	31.6
2	14	1	12.0	13.7
2	14	0	43.9	40.0
2	14	-1	20.0	16.4
2	14	-2	25.6	22.5
2	14	-4	15.6	12.3
2	14	-5	24.2	23.0
2	14	-6	28.3	28.5
2	14	-8	24.3	18.5
2	15	-2	19.9	16.7
2	15	-5	23.0	23.9
2	15	-6	20.4	19.3
2	15	-8	24.2	23.0
2	16	1	18.5	18.0
2	16	-1	17.7	17.8
2	16	-3	11.8	12.9
2	16	-4	11.6	12.7
2	16	-5	20.1	17.0
3	0	8	17.9	-15.6
3	0	6	17.1	17.4
3	0	2	16.9	-17.1
3	0	4	15.3	-6.1
3	0	-8	39.0	39.1
3	0	-10	44.5	-42.8
3	0	-12	88.3	84.3
3	1	8	21.4	18.4
3	1	7	20.2	-18.4
3	1	6	43.0	-40.1
3	1	4	42.7	41.9
3	1	1	48.9	50.6
3	1	-2	11.4	-19.8
3	1	-3	26.8	-18.1
3	1	-4	10.0	16.4
3	1	-5	11.5	-9.1
3	1	-6	23.8	-22.5
3	1	-7	6.8	7.7
3	1	-8	20.5	16.9
3	2	12	23.3	-19.3
3	2	10	14.7	-19.6
3	2	8	23.3	-19.3
3	2	7	24.4	-20.8
3	2	4	11.3	10.7
3	2	3	10.0	16.4
3	2	1	15.3	-14.6
3	2	0	12.9	-15.0
3	2	-1	66.4	64.0
3	2	-2	36.3	33.4
3	2	-3	8.5	4.6
3	2	-4	21.0	-23.3
3	2	-5	55.5	55.2
3	2	-6	61.0	51.8
3	2	-7	72.1	-66.7
3	2	-8	19.2	13.4
3	2	-9	41.3	40.6
3	2	-10	22.5	20.1
3	2	-11	60.8	-59.3
3	2	-12	40.2	-36.1
3	2	-13	22.4	21.2
3	2	-14	30.2	27.4
3	3	7	41.8	39.7
3	3	5	64.3	-54.2
3	3	4	15.3	-15.4
3	3	3	40.6	42.9
3	3	2	51.1	48.0
3	3	1	78.6	-98.0
3	3	0	33.2	25.7
3	3	-1	94.8	91.1
3	3	-2	22.7	20.5
3	3	-3	41.6	-29.8
3	3	-4	10.5	-9.6
3	3	-8	40.3	39.3
3	3	-6	30.1	27.2
3	3	-7	53.3	-44.9
3	3	-8	9.1	10.5
3	3	-11	11.7	-9.7
3	3	-14	16.0	-16.1
3	4	7	19.2	18.9
3	4	6	13.3	-12.2
3	4	5	22.0	-20.2
3	4	4	16.8	18.5
3	4	2	10.1	12.3
3	4	1	9.2	9.9
3	4	-1	43.5	-40.4
3	4	-2	6.3	-2.5
3	4	-3	28.7	24.3
3	4	-5	58.0	-52.9
3	4	-6	22.6	20.5
3	4	-7	96.4	83.6
3	4	-8	23.0	-19.1
3	4	-9	49.6	-49.3
3	4	-10	10.3	11.2
3	4	-11	31.7	28.9
3	4	-13	39.6	-33.9
3	5	8	22.8	-21.6
3	5	7	23.9	-21.9
3	5	6	44.7	46.4
3	5	5	52.3	52.9
3	5	4	45.9	-42.2
3	5	3	25.0	-22.7
3	5	2	39.8	44.2
3	5	1	74.0	83.6
3	5	0	19.4	-25.5
3	5	-1	47.9	-46.6
3	5	-2	27.6	28.4
3	5	-4	30.2	-24.9
3	5	-5	26.8	-23.7
3	5	-6	13.7	12.5
3	5	-8	17.6	-14.6
3	5	-10	18.4	17.8
3	6	8	14.4	-12.4
3	6	7	20.2	-19.5
3	6	6	29.4	24.0
3	6	4	31.0	-20.4
3	6	2	12.6	-11.3
3	6	1	11.8	-10.5
3	6	0	20.5	22.5
3	6	-2	11.1	4.6
3	6	-4	19.9	-8.7
3	6	-5	51.6	-40.9
3	6	-6	64.6	-53.8
3	6	-7	41.2	-36.9
3	6	-8	64.8	56.4
3	6	-9	41.5	40.9
3	6	-10	41.6	-42.1
3	6	-12	16.6	17.9
3	6	-13	19.1	18.5
3	7	8	21.5	21.5
3	7	7	16.2	14.0
3	7	6	50.8	-49.8
3	7	4	45.3	46.8

F OBS	F CALC	H	K	L	F OBS	F CALC
10,8	-11,9	4	1	-1	42,9	40,3
56,0	-57,2	4	1	-3	5,4	5,5
85,7	80,8	4	1	-4	33,2	-41,7
9,0	-4,6	4	1	-6	33,6	34,6
55,5	-57,9	4	1	-7	35,4	-36,2
66,9	5n,2	4	1	-8	75,2	-76,0
16,7	-8,1	4	1	-9	74,0	76,9
41,3	-35,7	4	1	-13	19,6	18,0
14,0	-15,9	4	2	6	20,1	22,3
30,3	25,7	4	2	5	36,9	-34,8
13,4	13,8	4	2	4	18,8	-18,4
18,0	-16,0	4	2	3	20,6	21,6
25,5	-25,1	4	2	2	26,0	29,3
33,7	-29,2	4	2	0	28,6	-26,0
9,5	9,2	4	2	-1	114,8	110,9
35,6	-29,5	4	2	-2	53,6	59,7
22,7	-21,4	4	2	-3	38,3	-30,5
25,7	23,0	4	2	-4	52,0	-39,4
55,7	4n,6	4	2	-5	31,3	29,1
32,3	-29,1	4	2	-6	25,8	20,6
44,2	-45,7	4	2	-7	28,0	-25,7
37,9	29,6	4	2	-8	9,1	29,9
15,1	21,4	4	2	12	13,3	-16,1
22,2	-20,4	4	2	13	13,9	-13,5
23,2	21,7	4	2	14	14,2	-13,7
21,3	19,8	4	3	5	12,2	-10,9
17,4	17,9	4	3	-1	50,4	48,9
22,7	25,3	4	3	-2	20,2	-19,4
30,2	-27,9	4	3	-3	56,7	53,2
22,5	-20,2	4	3	-4	28,6	27,3
35,4	33,6	4	3	-5	70,8	-69,8
14,6	14,8	4	3	-6	14,0	-10,7
52,3	-47,9	4	3	-7	71,0	62,1
40,4	-38,4	4	3	-9	31,0	-35,3
59,9	53,8	4	3	10	31,4	-27,3
10,3	7,7	4	3	11	26,0	27,1
30,1	-28,6	4	3	12	20,2	-20,8
15,8	16,2	4	3	13	32,9	-28,6
25,4	23,4	4	4	6	14,1	16,8
25,4	-22,7	4	4	5	18,7	19,7
16,5	-15,6	4	4	4	36,2	-34,0
22,2	21,7	4	4	3	48,5	-50,1
13,5	13,6	4	4	1	64,4	69,7
15,7	-16,8	4	4	0	25,6	-25,5
22,9	22,5	4	4	-1	36,4	-35,3
11,1	-10,3	4	4	-3	79,1	77,8
10,9	-11,8	4	4	-4	24,9	-22,8
26,5	27,0	4	4	-5	33,4	-28,8
41,9	-35,4	4	4	-6	7,5	8,4
39,4	33,6	4	4	-7	18,9	-16,5
24,3	-20,5	4	4	-8	10,2	-11,4
13,5	-11,5	4	4	10	12,1	12,2
27,2	23,6	4	4	12	18,1	19,3
10,8	14,7	4	4	13	12,2	15,9
39,0	-35,8	4	5	2	18,9	-18,6
15,6	-14,9	4	5	1	24,9	-23,4
11,7	11,6	4	5	0	15,5	13,9
26,9	26,3	4	5	-1	23,9	19,5
17,8	-19,0	4	5	-2	50,6	-49,9
40,5	-39,7	4	5	-3	63,4	-57,2
11,4	9,7	4	5	-4	28,3	27,1
42,3	46,0	4	5	-6	51,2	-43,6
42,7	-40,0	4	5	-7	8,8	2,9
22,0	24,1	4	5	-8	9,5	8,3
25,6	21,7	4	5	-9	53,8	50,6
11,5	-10,3	4	5	10	16,6	-14,9
11,8	11,8	4	5	11	22,1	-20,3
14,2	14,1	4	5	12	24,1	21,6
19,2	-19,7	4	5	13	28,4	24,3
15,8	-9,8	4	5	14	19,8	-21,2
11,3	8,4	4	6	4	33,8	31,0
11,6	-11,1	4	6	3	27,4	26,6
11,8	10,9	4	6	2	79,8	-76,1
15,2	15,6	4	6	1	53,9	-59,1
24,5	20,3	4	6	0	77,2	70,0
23,4	-26,4	4	6	-1	32,2	33,8
22,1	19,0	4	6	-2	77,1	-68,7
23,1	9,0	4	6	-3	14,4	-12,1
23,1	-25,9	4	6	-4	39,1	36,5
21,5	19,9	4	6	-6	17,5	-16,0
16,4	10,2	4	7	0	36,2	-38,1
32,6	-29,0	4	7	-2	37,1	34,5
27,0	-25,3	4	7	-4	41,1	-35,1
46,1	42,4	4	7	-7	27,2	-23,2
13,4	14,2	4	7	-8	47,2	-44,9
43,2	-40,5	4	7	-9	13,0	13,4
24,3	22,0	4	7	10	45,9	47,9
12,3	-11,9	4	7	12	17,4	-18,8
10,6	-12,6	4	8	2	45,2	44,1
21,5	20,7	4	8	1	31,0	27,8
15,5	-14,6	4	8	0	65,2	-59,5
14,3	14,7	4	8	-1	31,7	29,8
16,1	16,9	4	8	-2	58,9	47,2
14,4	-14,1	4	8	-3	32,6	-24,6
29,3	-26,9	4	8	-6	10,4	-10,6
23,8	26,7	4	8	-8	21,7	-19,4
13,3	-11,6	4	9	1	15,6	14,5
16,5	11,1	4	9	0	11,9	10,5
10,5	16,7	4	9	-2	16,4	-16,6
31,7	-10,0	4	9	-3	37,8	33,7
11,9	-31,2	4	9	-7	16,1	-16,9
23,1	15,0	4	9	-8	37,8	33,7
11,9	12,4	4	9	-4	29,6	26,1
12,2	-11,7	4	9	-5	23,4	-21,9
16,5	-15,9	4	9	-6	16,1	-15,6
12,3	13,9	4	9	-7	36,7	40,0
16,8	-50,0	4	9	-8	11,9	14,3
36,6	36,7	4	9	-9	43,6	-45,0
12,3	-21,5	4	9	12	15,5	16,1
9,7	11,9	4	10	5	17,5	18,0
12,3	-11,0	4	10	3	19,6	-17,9
35,3	-35,1	4	10	1	35,4	35,0

H	K	L	F OBS	F CALC
5	5	-7	14,4	-9,6
5	5	14	16,5	15,0
5	5	15	12,8	14,5
5	6	9	35,4	-34,9
5	6	-1	27,3	-26,3
5	6	-2	57,7	59,7
5	6	-3	44,7	44,3
5	6	-4	47,0	-42,8
5	6	-6	63,7	53,3
5	6	-7	32,3	30,4
5	6	-8	57,7	-53,3
5	6	-9	33,6	-29,4
5	6	10	35,0	32,6
5	6	11	24,2	-18,8
5	6	13	17,0	-16,8
5	6	14	25,0	24,3
5	7	4	34,4	27,1
5	7	1	19,4	-15,0
5	7	3	25,3	21,1
5	7	1	10,9	-10,2
5	7	0	34,7	-34,8
5	7	-1	23,3	-23,3
5	7	-2	70,6	77,0
5	7	-3	13,6	-13,4
5	7	-4	29,1	-26,5
5	7	-5	21,1	19,4
5	7	-7	13,0	12,4
5	7	13	10,8	-13,7
5	7	14	13,0	-12,7
5	8	1	24,1	20,4
5	8	0	24,4	22,3
5	8	2	37,6	-33,8
5	8	-4	43,8	37,8
5	8	-6	39,5	-33,3
5	8	-7	19,4	15,6
5	8	-9	49,2	52,6
5	8	-9	37,0	-31,8
5	8	11	16,0	16,9
5	8	13	13,5	-13,3
5	8	14	19,0	-21,8
5	9	5	24,1	24,6
5	9	3	23,9	-21,2
5	9	1	13,1	12,9
5	9	2	11,2	10,5
5	9	-1	25,9	-24,2
5	9	-2	21,9	-17,7
5	9	-3	39,1	34,8
5	9	-4	10,8	8,3
5	9	-5	24,4	-22,0
5	9	-8	17,1	16,3
5	9	-9	19,6	-17,5
5	10	11	14,3	-13,3
5	10	-1	21,6	16,9
5	10	-3	32,3	-28,0
5	10	-5	48,0	45,0
5	10	-7	54,2	-48,9
5	10	-9	30,5	28,3
5	10	10	11,0	-12,1
5	10	13	18,9	19,3
5	11	3	21,5	21,1
5	11	1	21,8	-17,0
5	11	-1	28,3	22,3
5	11	-2	21,6	-21,4
5	11	-3	24,4	-22,1
5	11	-5	16,0	14,4
5	11	-7	15,9	-17,6
5	12	0	17,4	-13,3
5	12	-1	12,6	-11,2
5	12	-4	25,7	-26,4
5	12	-5	27,9	-28,1
5	12	-6	30,5	26,1
5	12	-8	23,0	-20,1
5	12	-9	22,3	-18,3
5	12	13	16,9	15,5
5	12	11	11,7	12,9
5	12	12	13,9	-14,6
5	13	2	18,7	16,8
5	13	1	12,1	11,2
5	13	0	22,0	-21,3
5	13	22	22,5	20,2
5	13	-4	10,6	-11,6
5	13	-5	12,2	-12,4
6	0	6	32,3	30,7
6	0	4	15,2	-13,0
6	0	0	47,8	-52,1
6	0	10	19,6	-17,0
6	0	12	26,3	24,6
6	1	1	10,8	9,9
6	1	0	22,1	23,8
6	1	-1	28,5	-30,9
6	1	-2	42,7	-44,4
6	1	-4	10,4	13,2
6	1	-5	6,1	-1,8
6	1	-6	16,1	-27,2
6	1	-7	21,4	19,6
6	1	-8	60,5	69,1
6	1	-9	37,8	-36,8
6	1	10	47,3	-51,4
6	1	11	18,6	18,9
6	1	12	35,5	36,5
6	1	13	16,7	-14,3
6	1	14	16,7	-15,5
6	2	6	18,7	-16,7
6	2	5	31,1	31,2
6	2	4	11,6	7,8
6	2	3	19,3	-16,9
6	2	2	18,8	-13,9
6	2	1	14,1	9,9

H	K	L	F OBS	F CALC
6	2	0	18,4	16,9
6	2	-1	92,6	-89,9
6	2	-2	9,4	-6,8
6	2	-3	13,5	11,3
6	2	-4	15,0	15,7
6	2	-5	6,5	-7,2
6	2	-6	21,7	-18,0
6	2	-8	11,4	7,7
6	2	10	13,0	9,9
6	2	13	11,8	11,2
6	2	14	15,2	15,6
6	3	1	15,7	-13,4
6	3	-1	27,6	27,4
6	3	-3	30,8	-30,9
6	3	-4	17,2	-17,5
6	3	-5	47,9	49,5
6	3	-6	11,0	5,6
6	3	-7	66,3	-60,8
6	3	-8	8,7	8,9
6	3	10	24,0	19,2
6	3	11	41,0	-37,5
6	3	13	20,5	18,0
6	4	5	25,9	-26,7
6	4	4	14,9	14,5
6	4	3	32,8	28,9
6	4	-2	14,3	-12,8
6	4	1	39,3	36,2
6	4	-3	22,5	-19,0
6	4	-5	30,2	26,4
6	4	-6	8,2	9,7
6	4	-7	18,8	-15,8
6	4	12	11,7	-10,7
6	5	1	18,9	14,0
6	5	-2	18,3	12,6
6	5	-3	12,3	11,7
6	5	-4	28,6	-24,6
6	5	-5	44,4	-40,2
6	5	-6	61,4	55,4
6	5	-7	56,4	52,0
6	5	-8	44,5	-40,7
6	5	-9	42,4	-41,0
6	5	10	30,8	28,7
6	5	11	26,7	24,3
6	5	12	20,6	-19,3
6	5	13	11,8	-14,1
6	6	4	22,1	-20,8
6	6	3	11,6	8,4
6	6	2	32,8	28,4
6	6	1	21,5	-19,1
6	6	0	21,0	-18,7
6	6	-1	14,3	9,4
6	6	-4	20,9	-13,9
6	6	-5	17,2	-12,9
6	6	-6	18,3	16,0
6	6	11	20,4	-17,9
6	7	2	11,7	8,9
6	7	0	17,9	15,8
6	7	-1	18,8	-13,8
6	7	-3	24,5	22,0
6	7	-4	33,5	29,7
6	7	-5	15,2	12,5
6	7	-6	52,8	-50,1
6	7	-7	19,0	-14,5
6	7	-8	55,0	59,9
6	7	10	43,4	-47,1
6	7	12	11,8	13,1
6	8	4	17,3	17,1
6	8	3	14,1	-11,5
6	8	2	29,6	-25,4
6	8	1	27,2	23,5
6	8	0	24,7	20,7
6	8	-1	22,6	-19,5
6	8	-2	14,8	11,4
6	8	-6	20,7	-18,9
6	8	-8	13,4	12,5
6	9	1	19,9	-16,6
6	9	0	11,8	-10,3
6	9	-1	23,7	20,3
6	9	-3	24,5	-22,6
6	9	-5	26,2	21,5
6	9	-6	30,3	-26,7
6	9	-7	34,0	-32,0
6	9	-8	29,0	-26,9
6	9	-9	36,8	-36,9
6	10	1	20,0	-19,7
6	10	-1	22,3	20,7
6	10	-3	16,7	-14,6
6	10	-7	11,8	-12,0
6	11	1	10,2	9,4
6	11	0	12,4	-12,5
6	11	-1	22,3	-20,5
6	11	-3	14,9	13,4
6	11	-4	19,0	17,0
6	11	-5	21,3	-18,8
6	11	-6	21,3	18,9
6	11	-7	32,0	30,3
6	11	-9	30,9	-29,1
6	12	1	20,7	-19,5
6	12	-1	20,7	-19,5
6	12	-2	17,5	16,0
6	12	-4	12,6	-13,8
6	13	-2	13,7	-14,0
6	13	-3	10,0	9,7
6	13	-6	10,2	10,7
6	13	-6	19,5	-20,4
7	0	2	13,3	-12,0
7	0	0	19,2	-14,3
7	0	-2	29,8	-22,7

H	K	L	F OBS	F CALC
7	0	-8	43,9	54,8
7	0	10	10,8	-10,9
7	0	12	35,0	33,0
7	0	14	27,4	-30,8
7	1	4	24,3	24,6
7	1	3	11,1	-9,8
7	1	2	22,0	-20,9
7	1	0	20,3	19,1
7	1	-1	29,5	-24,1
7	1	-2	23,9	-18,0
7	1	-4	7,0	9,1
7	1	-9	9,6	9,4
7	1	12	12,8	-13,1
7	1	13	13,3	12,6
7	1	14	24,9	23,5
7	2	1	14,0	-19,4
7	2	-1	35,2	33,4
7	2	12	22,6	19,8
7	2	13	24,9	-20,5
7	2	-4	21,8	-23,3
7	2	-5	21,9	24,2
7	2	-6	25,9	25,2
7	2	-7	42,7	-38,3
7	2	-8	35,4	-28,8
7	2	-9	36,4	31,2
7	2	10	16,9	14,7
7	2	11	16,2	-15,3
7	2	13	25,7	24,9
7	3	-4	14,8	17,8
7	3	-5	16,1	-21,0
7	3	13	24,9	-21,3
7	3	11	25,8	-21,9
7	3	-1	31,9	25,0
7	3	-3	16,2	-12,3
7	3	-5	11,1	10,2
7	3	-9	13,2	-11,0
7	3	12	16,0	-16,0
7	3	13	24,9	-21,3
7	3	14	11,4	-13,3
7	3	15	22,7	23,0
7	4	1	16,3	14,0
7	4	-1	36,3	-33,4
7	4	-3	40,7	42,9
7	4	-6	19,5	17,9
7	4	-7	35,6	29,2
7	4	-9	56,9	-52,1
7	4	11	33,9	29,5
7	4	12	20,9	-20,0
7	4	13	21,1	-19,2
7	5	15	19,4	21,1
7	5	4	15,6	-14,7
7	5	3	14,5	14,8
7	5	2	18,7	15,5
7	5	0	13,3	-12,1
7	5	-1	26,2	-23,6
7	5	-2	14,2	10,2
7	5	-3	12,8	11,1
7	5	-4	24,8	-21,8
7	5	-9	12,2	12,8
7	5	11	13,1	-12,7
7	5	12	11,5	10,9
7	5	14	20,2	-22,8
7	5	15	18,8	-24,5
7	6	2	10,7	-8,7
7	6	0	25,8	22,8
7	6	-1	16,3	15,9
7	6	-2	34,6	-31,5
7	6	-3	18,1	-13,9
7	6	-5	36,1	-34,4
7	6	-8	34,6	32,5
7	6	-9	45,1	48,3
7	6	10	47,1	-50,3
7	6	12	16,3	20,3
7	6	13	11,3	12,1
7	6	14	17,6	-19,7
7	7	2	18,7	-18,4
7	7	0	25,4	25,0
7	7	-2	38,2	-33,8
7	7	-3	11,4	9,2
7	7	-4	11,2	7,5
7	7	-5	11,1	-8,2
7	7	-7	24,0	-20,0
7	7	11	14,9	12,5
7	7	11	11,5	11,2
7	8	0	22,1	-20,9
7	8	-1	16,1	12,5
7	8	-2	37,0	30,8
7	8	-3	20,0	-17,8
7	8	-4	21,0	-16,4
7	8	-5	20,9	17,5
7	8	-6	11,4	-9,7
7	8	-7	20,9	-20,0
7	8	-8	37,0	-32,6
7	8	-9	24,0	22,1
7	8	-10	32,6	33,9
7	8	-11	11,4	-12,7
7	8	-12	12,8	-12,0
7	9	1	13,8	-13,0
7	9	0	10,5	-8,9
7	9	-1	17,9	19,2
7	9	-2	14,6	11,5
7	9	-3	20,9	-20,2
7	10	-1	16,9	-15,2
7	10	-3	23,9	21,4
7	10	-5	24,1	-24,5
7	10	-7	26,9	28,1
7	10	-9	27,1	-28,2
7	10	11	13,2	12,4

TABLE 28

$Cu(\alpha\text{-pic})_2(NO_3)_2$ - Form I

Atom positions (fractional coordinates)

	x/a	y/b	z/c
Cu	0.25231(34)	0.65976(14)	0.28040(18)
C(1)	0.2258(21)	0.4774(10)	0.3445(12)
C(2)	0.2249(24)	0.3834(10)	0.3431(13)
C(3)	0.2363(30)	0.3413(11)	0.2626(14)
C(4)	0.2409(27)	0.3898(10)	0.1878(16)
C(5)	0.2473(26)	0.4817(12)	0.1964(13)
C(6)	0.2179(26)	0.5281(12)	0.4292(11)
C(7)	0.2794(27)	0.8369(12)	0.3762(15)
C(8)	0.2873(28)	0.9301(11)	0.3786(17)
C(9)	0.2858(25)	0.9764(11)	0.3006(17)
C(10)	0.2644(31)	0.9311(11)	0.2157(18)
C(11)	0.2515(30)	0.8385(12)	0.2102(15)
C(12)	0.2789(34)	0.7813(13)	0.4600(16)
O(1)	0.0301(20)	0.6606(10)	0.0856(10)
O(2)	-0.2693(21)	0.6522(12)	0.0362(13)
O(3)	-0.0386(23)	0.6618(9)	0.2041(11)
O(4)	0.5343(18)	0.6528(8)	0.3947(9)
O(5)	0.7986(19)	0.6503(10)	0.3983(12)
O(6)	0.5183(21)	0.6636(8)	0.2487(11)
N(1)	0.2415(21)	0.5248(8)	0.2745(11)
N(2)	0.2625(20)	0.7924(8)	0.2936(11)
N(3)	-0.0930(21)	0.6582(10)	0.1035(11)
N(4)	0.6284(22)	0.6551(10)	0.3483(12)

TABLE 29

$Cu(\alpha\text{-pic})_2(NO_3)_2$ - Form I

(a) Anisotropic temperature factors ($Å^2$) *

	U_{11}	U_{22}	U_{33}	$2U_{32}$	$2U_{31}$	$2U_{12}$
Cu	0.041	0.032	0.043	0.000	0.052	0.001
C(1)	0.013	0.029	0.035	-0.016	0.033	0.005
C(2)	0.023	0.024	0.037	0.005	0.022	-0.009
C(3)	0.062	0.033	0.047	-0.007	0.072	-0.017
C(4)	0.042	0.019	0.068	-0.020	0.079	-0.012
C(5)	0.034	0.044	0.039	-0.015	0.048	0.019
C(6)	0.049	0.057	0.016	-0.015	0.029	-0.021
C(7)	0.040	0.037	0.045	0.006	0.050	0.001
C(8)	0.040	0.028	0.068	-0.019	0.052	-0.005
C(9)	0.018	0.031	0.085	-0.002	0.077	-0.009
C(10)	0.065	0.033	0.068	0.006	0.085	-0.007
C(11)	0.060	0.046	0.034	0.007	0.065	-0.004
C(12)	0.075	0.047	0.050	0.013	0.084	0.026
O(1)	0.046	0.071	0.044	0.016	0.050	0.001
O(2)	0.030	0.094	0.071	0.019	0.033	0.002
O(3)	0.089	0.036	0.066	-0.008	0.097	0.005
O(4)	0.052	0.041	0.027	0.004	0.049	0.006
O(5)	0.032	0.061	0.073	0.020	0.056	0.021
O(6)	0.066	0.038	0.061	-0.007	0.091	-0.016
N(1)	0.040	0.019	0.038	-0.008	0.054	-0.010
N(2)	0.034	0.025	0.040	-0.006	0.058	0.004
N(3)	0.039	0.034	0.036	0.014	0.031	0.007
N(4)	0.030	0.054	0.049	0.004	0.056	-0.005

(b) Mean estimated standard deviations ($Å^2$)

Cu	0.001	0.001	0.001	0.002	0.002	0.003
C	0.011	0.009	0.010	0.016	0.019	0.018
O	0.008	0.007	0.007	0.011	0.012	0.013
N	0.009	0.007	0.007	0.012	0.014	0.014

* These are the values of U_{ij} in equation (5) (Section I.1.4(b)).

TABLE 30

$Cu(\alpha\text{-pic})_2(NO_3)_2$ - Form II

Cu	0.26598(22)	0.17595(10)	0.23196(14)
C(1)	0.6225(18)	0.2636(9)	0.3095(10)
C(2)	0.8017(19)	0.2660(10)	0.3557(12)
C(3)	0.9004(19)	0.1857(11)	0.3935(12)
C(4)	0.8118(20)	0.1035(10)	0.3827(14)
C(5)	0.6241(20)	0.1046(9)	0.3373(12)
C(6)	0.5110(21)	0.3495(8)	0.2672(14)
C(7)	-0.0766(17)	0.2732(8)	0.1499(10)
C(8)	-0.2613(19)	0.2813(10)	0.0969(11)
C(9)	-0.3711(19)	0.2031(11)	0.0636(12)
C(10)	-0.2862(20)	0.1201(11)	0.0801(13)
C(11)	-0.1072(20)	0.1129(9)	0.1310(13)
C(12)	0.0421(21)	0.3547(9)	0.1861(14)
O(1)	0.2463(17)	0.0478(7)	0.1059(10)
O(2)	0.2090(16)	0.1073(8)	-0.0456(9)
O(3)	0.2415(12)	0.1955(6)	0.0870(7)
O(4)	0.2959(13)	0.1678(6)	0.3809(9)
O(5)	0.2935(16)	0.0603(9)	0.4845(10)
O(6)	0.2695(15)	0.0256(7)	0.3271(9)
N(1)	0.5327(13)	0.1835(7)	0.2991(8)
N(2)	0.0003(14)	0.1889(6)	0.1664(8)
N(3)	0.2344(15)	0.1142(7)	0.0460(9)
N(4)	0.2863(16)	0.0807(8)	0.3995(9)

TABLE 31

$Cu(\alpha\text{-pic})_2(NO_3)_2$ - Form II

(a) Anisotropic temperature factors ($\AA^2$) *

	$\underline{U}_{11}$	$\underline{U}_{22}$	$\underline{U}_{33}$	$2\underline{U}_{32}$	$2\underline{U}_{31}$	$2\underline{U}_{12}$
Cu	0.037	0.025	0.047	0.002	0.049	-0.001
C(1)	0.041	0.032	0.035	0.005	0.042	-0.010
C(2)	0.039	0.062	0.059	-0.031	0.073	-0.044
C(3)	0.038	0.066	0.045	-0.015	0.052	-0.013
C(4)	0.033	0.047	0.076	0.001	0.061	0.024
C(5)	0.052	0.028	0.059	0.013	0.074	0.029
C(6)	0.053	0.017	0.086	0.018	0.047	-0.011
C(7)	0.040	0.023	0.044	-0.007	0.059	0.013
C(8)	0.048	0.042	0.042	-0.002	0.054	0.011
C(9)	0.032	0.071	0.046	0.001	0.040	0.002
C(10)	0.037	0.052	0.069	0.009	0.059	-0.013
C(11)	0.046	0.021	0.076	0.005	0.076	-0.004
C(12)	0.050	0.026	0.087	-0.009	0.079	0.014
O(1)	0.086	0.039	0.074	0.025	0.091	0.007
O(2)	0.079	0.065	0.048	-0.022	0.086	-0.034
O(3)	0.044	0.038	0.044	0.008	0.056	0.006
O(4)	0.044	0.040	0.041	0.010	0.040	-0.007
O(5)	0.081	0.076	0.073	0.072	0.090	0.039
O(6)	0.066	0.040	0.069	0.024	0.081	-0.019
N(1)	0.032	0.026	0.038	0.006	0.047	-0.002
N(2)	0.030	0.028	0.037	0.008	0.043	0.008
N(3)	0.043	0.038	0.042	0.000	0.056	0.003
N(4)	0.039	0.052	0.047	0.050	0.055	0.007

(b) Mean estimated standard deviations ($\AA^2$)

Cu	0.001	0.001	0.001	0.002	0.001	0.002
C	0.008	0.008	0.009	0.012	0.014	0.012
O	0.008	0.006	0.007	0.010	0.012	0.010
N	0.007	0.006	0.006	0.010	0.010	0.009

* These are the values of U_{ij} in equation (5) (Section I.1.4(b)).

APPENDIX VII

EXPERIMENTAL

AQUO(DINITRATOBISQUINOLINE)-CADMIUM(II)

Preparation of Crystals

Crystals of $Cd(quin)_2(NO_3)_2(H_2O)$ were prepared from a 1:1 solution of ethanol-2,2-dimethoxypropane containing stoicheiometric amounts of $Cd(NO_3)_2.4H_2O$ and quinoline. The crystals are colourless needles with the needle-axis corresponding to b. To avoid atmospheric decomposition in the X-ray beam, the crystals were enclosed in thin-walled glass tubes.

Crystal Data

$C_{18}H_{16}N_4O_7Cd$

M = 512.8

Monoclinic

a = 11.018 ± 0.005, b = 8.585 ± 0.005, c = 23.756 ± 0.009 Å, β = 91.07 ± 0.02°, U = 2247 Å^3

D_m = 1.51, Z = 4, D_c = 1.52

F(000) = 1024

Space group $P2_1/c$ (C_{2h}^5, No 14) from systematic absences: 0k0 for k odd, h0ℓ for ℓ odd

Mo-K_α X-rays, λ = 0.7107 Å

μ(Mo-K_α) = 10.1 cm^{-1}

Crystallographic Measurements

The unit-cell parameters were initially determined from oscillation and Weissenberg photographs taken with Cu-K_α radiation (λ = 1.5418 Å), and from precession photographs taken with Mo-K_α radiation. These were subsequently adjusted by least-squares refinement of θ, χ, and ϕ setting angles of twelve reflections determined on a Hilger and Watts Y 290 diffractometer.

For the intensity measurements, zirconium-filtered molybdenum radiation was used and 3922 reflections were collected by use of the θ to 2θ scan technique. Of these some 3697 reflections were considered observed using the criteria $I \geqslant 1\sigma(I)$, where σ was determined from counter statistics. Values of I were corrected for Lorentz-polarisation effects but no corrections for absorption were made.

Structure Determination and Refinement

The entire structure was determined by conventional Patterson and electron-density calculations with initial phasing appropriate to the cadmium atom. Several cycles of structure-factor and electron-density calculations effected preliminary refinement and reduced R to 0.23. During these preliminary calculations an

overall isotropic vibration parameter, U_{iso} (0.06 Å^2), was assigned to the atoms.

The least-squares refinement of positional, thermal, and scale parameters converged after 11 cycles, when R was 0.08 and R' was 0.011. Removal of those planes for which $I \geqslant 2\sigma(I)$ left 3029 independent data, and a structure-factor calculation using the final parameters resulted in R 0.06 and R' 0.008. After cycle 5, a difference Fourier synthesis was calculated which revealed positions for all the hydrogen atoms. In subsequent cycles these were refined using isotropic temperature factors (for details of the refinement see Table 32).

The refinement of anisotropic thermal parameters necessitated the use of the block-diagonal approximation to the normal-equation matrix because of computer-store limitations.

In all refinement cycles, the weighting scheme given as equation (32) (Section I.1.8(b)) was applied to the data. Initially the parameters p were chosen to give unit weight to all reflections, but they were varied in later cycles as indicated by a $|F_o|$ and $(\sin\theta/\lambda)$ analysis of $\sum w\Delta^2$. The final values are p_1 50, p_2 0.001, p_3 0.01, p_4 0.

At the conclusion of the refinement a difference synthesis and final electron-density distribution

were calculated. These revealed no errors in the structure.

In all the structure-factor calculations, the atomic scattering factors used are those given in ref. 212. The observed and calculated structure factors are listed in Table 33. Fractional coordinates of all non-hydrogen atoms are given in Table 34, and anisotropic thermal parameters in Table 35. The positions of the hydrogen atoms and their isotropic thermal parameters are given in Table 36.

The relevant interatomic dimensions and some calculated least-squares best planes through the molecule are given in Section III.2.2. The estimated standard deviations recorded were derived from the inverse of the least-squares normal-equation matrix, and are probably best regarded as minimum values.

TABLE 32

$Cd(quin)_2(NO_3)_2(H_2O)$

Course of refinement

Cycles	Parameters refined	Final R	Final R'
1-4	x, y, z, U_{iso} for Cd, N, O, C; layer scale-factors, unit weights, full matrix	0.114	0.0433
5-6	x, y, z, U_{iso} for Cd, N, O, C; layer scale-factors, weighting scheme adjusted, full matrix	0.103	0.0372
7-8	x, y, z, U_{iso} for Cd, N, O, C, H; one overall scale-factor, weighting scheme adjusted, full matrix	0.100	0.0298
9-11	x, y, z, $U_{ij}(i,j = 1,2,3)$ for Cd, N, O, C; x, y, z, U_{iso} for H; small adjustments to weighting scheme, block-diagonal approximation to normal-equation matrix	0.078	0.0112
12	Planes for which $I \leqslant 2\sigma(I)$ removed	0.060	0.0081

TABLE 33

$Cd(quin)_2(NO_3)_2(H_2O)$

Observed and final-calculated structure amplitudes

H	K	L	F OBS	F CALC
13	1	1	11.9	13.8
13	1	2	14.4	15.6
13	1	3	13.5	9.5
12	2	2	12.6	12.4
12	2	3	20.6	-15.4
12	2	4	14.7	-17.8
12	2	5	23.2	22.9
12	2	6	26.3	-12.4
12	2	7	14.3	-27.5
12	2	8	18.0	-33.2
12	2	9	19.3	-27.4
12	2	10	22.9	21.5
12	3	1	16.7	23.1
12	3	2	14.0	12.5
12	3	3	24.6	-37.7
12	3	4	16.7	27.4
12	3	5	18.0	-13.1
12	3	6	24.4	-22.4
12	3	7	18.7	21.7
12	3	8	24.6	32.9
12	4	1	10.7	9.7
12	4	2	24.2	22.2
12	4	3	24.8	-27.8
12	4	4	19.8	30.9
12	4	5	24.5	-27.0
12	4	6	29.5	31.9
12	4	7	26.7	-25.2
12	5	1	21.9	23.3
12	5	2	20.6	21.5
12	5	3	10.7	13.0
12	5	4	20.6	21.5
12	5	5	15.5	-17.0
12	6	1	19.2	23.3
12	6	2	22.5	-22.4
12	6	3	19.1	-16.1
12	6	4	14.6	-21.9
12	7	1	14.9	15.2
12	7	2	19.3	12.4
12	8	1	12.0	-16.1
11	1	1	11.9	13.8
11	1	2	19.5	-19.9
11	1	3	19.3	9.5
11	1	4	30.4	31.9
11	1	5	18.5	-23.3
11	1	6	23.1	-7.7
11	1	7	18.8	32.9
11	1	8	31.5	31.9
11	1	9	19.9	19.9
11	1	10	16.7	23.1
11	2	1	14.0	12.5
11	2	2	24.6	-37.7
11	2	3	24.7	27.4
11	2	4	24.8	-27.8
11	2	5	19.8	30.9
11	2	6	24.5	-27.0
11	2	7	29.5	31.9
11	2	8	26.7	-25.2
11	3	1	29.5	31.9
11	3	2	24.2	-27.4
11	3	3	36.8	34.3
11	3	4	16.0	-10.4
11	3	5	17.4	-14.8
11	3	6	29.7	32.9
11	3	7	28.1	27.1
11	3	8	32.1	-32.3
11	4	1	17.7	15.4
11	4	2	32.0	31.5
11	4	3	11.0	-11.4
11	4	4	15.2	-11.9
11	4	5	29.7	32.9
11	4	6	29.3	-22.0
11	4	7	37.1	39.4
11	5	1	53.8	49.7
11	5	2	30.0	-32.7
11	5	3	57.1	-57.7
11	5	4	12.1	14.7
11	5	5	24.1	25.9
11	5	6	46.8	47.5
11	6	1	46.4	-43.8
11	6	2	70.3	-74.5
11	6	3	21.6	-19.6
11	6	4	29.8	25.9
11	6	5	28.5	26.1
11	7	1	10.3	10.1
11	7	2	29.2	-32.0
11	7	3	31.7	-33.6
11	7	4	45.5	50.7
11	8	1	39.2	42.5
11	8	2	43.6	-59.0
11	8	3	45.6	-44.6
11	9	1	40.7	38.0
11	9	2	19.0	16.3
11	9	3	9.4	10.3
11	10	1	24.6	-29.8
11	10	2	13.6	-10.0
11	11	1	55.8	57.3
11	11	2	24.5	30.7
11	12	1	20.8	-21.0
11	13	1	9.7	4.7
10	1	1	17.1	-14.4
10	1	2	63.9	64.5
10	1	3	21.2	25.3
10	1	4	50.6	-44.0
10	1	5	22.3	-20.3
10	1	6	11.6	9.5
10	1	7	34.9	37.9
10	1	8	11.9	8.3
10	1	9	69.7	-68.2
10	1	10	36.6	-31.8
10	2	1	34.9	-35.6
10	2	2	35.1	37.1
10	2	3	35.1	-36.3
10	2	4	29.1	27.9
10	2	5	16.7	-19.1
10	2	6	78.1	-73.0
10	2	7	40.6	39.2
10	2	8	94.1	-89.7
10	2	9	74.9	85.5
10	2	10	16.7	-19.1
10	3	1	27.8	-28.2
10	3	2	28.4	-22.7
10	3	3	22.0	25.2
10	3	4	16.8	15.0
10	3	5	38.5	39.5
10	3	6	12.0	10.9
10	3	7	15.4	-9.7
10	3	8	18.4	-20.7
10	3	9	14.0	-12.5
10	3	10	18.3	17.2
10	4	1	30.4	28.5
10	4	2	54.9	-54.2
10	4	3	37.0	34.2
10	4	4	13.7	-13.1
10	4	5	16.8	19.2
10	4	6	47.3	-52.1
10	4	7	52.2	54.6
10	5	1	11.5	-12.0
10	5	2	25.0	-25.4
10	5	3	17.2	-20.3
10	5	4	43.8	-50.4
10	5	5	33.1	31.9
10	6	1	12.9	-13.9
10	6	2	48.8	-44.2
10	6	3	22.7	19.2
10	7	1	19.3	23.4
10	7	2	49.7	-42.4
9	1	1	24.5	27.0
9	1	2	18.5	-19.9
9	1	3	30.4	31.9
9	1	4	17.0	19.8
9	1	5	26.1	24.3
9	1	6	19.9	19.8
9	1	7	37.6	38.5
9	1	8	17.3	11.9
9	1	9	37.1	39.4
9	1	10	17.1	-14.4
9	1	11	32.3	-32.5
9	1	12	20.6	-20.3
9	2	1	21.2	25.3
9	2	2	50.6	-44.0
9	2	3	22.3	-20.3
9	2	4	11.6	9.5
9	2	5	34.9	37.9
9	2	6	11.9	8.3
9	2	7	32.0	31.8
9	2	8	25.6	-25.8
9	2	9	24.1	21.7
9	2	10	20.3	-18.6
9	2	11	25.6	-18.1
9	2	12	28.0	29.8
9	3	1	28.6	26.0
9	3	2	20.8	-22.4
9	3	3	11.8	-10.9
9	3	4	23.8	22.2
9	3	5	18.8	15.9
9	3	6	18.7	-15.9
9	3	7	23.8	22.2
9	3	8	13.5	-12.0
9	3	9	20.9	-19.1
9	3	10	15.2	12.9
9	4	1	33.6	30.4
9	4	2	15.9	-17.4
9	4	3	20.0	14.8
9	4	4	30.4	28.5
9	4	5	54.9	-54.2
9	4	6	37.0	34.2
9	4	7	13.7	-13.1
9	4	8	16.8	19.2
9	4	9	47.3	-52.1
9	4	10	52.2	54.6
9	5	1	22.7	19.2
9	5	2	19.3	23.4
9	5	3	49.7	-42.4
9	5	4	15.8	13.9
9	5	5	43.2	41.3
9	5	6	21.2	-18.9
9	5	7	12.2	11.8
9	5	8	24.3	-27.0
9	5	9	24.1	21.7
9	5	10	20.3	-18.6
9	5	11	25.6	-18.1
9	5	12	28.0	29.8
9	6	1	28.6	26.0
9	6	2	20.8	-22.4
9	6	3	11.8	-10.9
9	6	4	23.8	22.2
9	6	5	18.8	15.9
9	6	6	18.7	-15.9
9	6	7	23.8	22.2
9	6	8	13.5	-12.0
9	6	9	20.9	-19.1
9	6	10	15.2	12.9
9	7	1	33.6	30.4
9	7	2	15.9	-17.4
9	7	3	20.0	14.8
9	7	4	30.4	28.5
9	7	5	54.9	-54.2
9	7	6	37.0	34.2
9	7	7	13.7	-13.1
9	7	8	16.8	19.2
9	7	9	47.3	-52.1
9	7	10	52.2	54.6
9	8	1	22.7	19.2
9	8	2	19.3	23.4
9	8	3	49.7	-42.4
9	8	4	15.8	13.9
9	8	5	43.2	41.3
9	8	6	21.2	-18.9
9	8	7	12.2	11.8
9	8	8	24.3	-27.0
9	8	9	24.1	21.7
9	8	10	20.3	-18.6
9	8	11	25.6	-18.1
9	8	12	28.0	29.8
9	9	1	28.6	26.0
9	9	2	20.8	-22.4
9	9	3	11.8	-10.9
9	9	4	23.8	22.2
9	9	5	18.8	15.9
9	9	6	18.7	-15.9
9	9	7	23.8	22.2
9	9	8	13.5	-12.0
9	9	9	20.9	-19.1
9	9	10	15.2	12.9
9	10	1	33.6	30.4
9	10	2	15.9	-17.4
9	10	3	20.0	14.8
9	10	4	30.4	28.5
9	10	5	54.9	-54.2
9	10	6	37.0	34.2
9	10	7	13.7	-13.1
9	10	8	16.8	19.2
9	10	9	47.3	-52.1
9	10	10	52.2	54.6
9	11	1	22.7	19.2
9	11	2	19.3	23.4
9	11	3	49.7	-42.4
9	11	4	15.8	13.9
9	11	5	43.2	41.3
9	11	6	21.2	-18.9
9	11	7	12.2	11.8
9	11	8	24.3	-27.0
9	11	9	24.1	21.7
9	11	10	20.3	-18.6
9	11	11	25.6	-18.1
9	11	12	28.0	29.8
9	12	1	28.6	26.0
9	12	2	20.8	-22.4
9	12	3	11.8	-10.9
9	12	4	23.8	22.2
9	12	5	18.8	15.9
9	12	6	18.7	-15.9
9	12	7	23.8	22.2
9	12	8	13.5	-12.0
9	12	9	20.9	-19.1
9	12	10	15.2	12.9
9	13	1	33.6	30.4
9	13	2	15.9	-17.4
9	13	3	20.0	14.8
9	13	4	30.4	28.5
9	13	5	54.9	-54.2
9	13	6	37.0	34.2
9	13	7	13.7	-13.1
9	13	8	16.8	19.2
9	13	9	47.3	-52.1
9	13	10	52.2	54.6
9	14	1	22.7	19.2
9	14	2	19.3	23.4
9	14	3	49.7	-42.4
9	14	4	15.8	13.9
9	14	5	43.2	41.3
9	14	6	21.2	-18.9
9	14	7	12.2	11.8
9	14	8	24.3	-27.0
9	14	9	24.1	21.7
9	14	10	20.3	-18.6
9	14	11	25.6	-18.1
9	14	12	28.0	29.8
9	15	1	28.6	26.0
9	15	2	20.8	-22.4
9	15	3	11.8	-10.9
9	15	4	23.8	22.2
9	15	5	18.8	15.9
9	15	6	18.7	-15.9
9	15	7	23.8	22.2
9	15	8	13.5	-12.0
9	15	9	20.9	-19.1
9	15	10	15.2	12.9
9	16	1	33.6	30.4
9	16	2	15.9	-17.4
9	16	3	20.0	14.8
9	16	4	30.4	28.5
9	16	5	54.9	-54.2
9	16	6	37.0	34.2
9	16	7	13.7	-13.1
9	16	8	16.8	19.2
9	16	9	47.3	-52.1
9	16	10	52.2	54.6
9	17	1	22.7	19.2
9	17	2	19.3	23.4
9	17	3	49.7	-42.4
9	17	4	15.8	13.9
9	17	5	43.2	41.3
9	17	6	21.2	-18.9
9	17	7	12.2	11.8
9	17	8	24.3	-27.0
9	17	9	24.1	21.7
9	17	10	20.3	-18.6
9	17	11	25.6	-18.1
9	17	12	28.0	29.8
9	18	1	28.6	26.0
9	18	2	20.8	-22.4
9	18	3	11.8	-10.9
9	18	4	23.8	22.2
9	18	5	18.8	15.9
9	18	6	18.7	-15.9
9	18	7	23.8	22.2
9	18	8	13.5	-12.0
9	18	9	20.9	-19.1
9	18	10	15.2	12.9
9	19	1	33.6	30.4
9	19	2	15.9	-17.4
9	19	3	20.0	14.8
9	19	4	30.4	28.5
9	19	5	54.9	-54.2
9	19	6	37.0	34.2
9	19	7	13.7	-13.1
9	19	8	16.8	19.2
9	19	9	47.3	-52.1
9	19	10	52.2	54.6
9	20	1	22.7	19.2
9	20	2	19.3	23.4
9	20	3	49.7	-42.4
9	20	4	15.8	13.9
9	20	5	43.2	41.3
9	20	6	21.2	-18.9
9	20	7	12.2	11.8
9	20	8	24.3	-27.0
9	20	9	24.1	21.7
9	20	10	20.3	-18.6
9	20	11	25.6	-18.1
9	20	12	28.0	29.8
9	21	1	28.6	26.0
9	21	2	20.8	-22.4
9	21	3	11.8	-10.9
9	21	4	23.8	22.2
9	21	5	18.8	15.9
9	21	6	18.7	-15.9
9	21	7	23.8	22.2
9	21	8	13.5	-12.0
9	21	9	20.9	-19.1
9	21	10	15.2	12.9
9	22	1	33.6	30.4
9	22	2	15.9	-17.4
9	22	3	20.0	14.8
9	22	4	30.4	28.5
9	22	5	54.9	-54.2
9	22	6	37.0	34.2
9	22	7	13.7	-13.1
9	22	8	16.8	19.2
9	22	9	47.3	-52.1
9	22	10	52.2	54.6
9	23	1	22.7	19.2
9	23	2	19.3	23.4
9	23	3	49.7	-42.4
9	23	4	15.8	13.9
9	23	5	43.2	41.3
9	23	6	21.2	-18.9
9	23	7	12.2	11.8
9	23	8	24.3	-27.0
9	23	9	24.1	21.7
9	23	10	20.3	-18.6
9	23	11	25.6	-18.1
9	23	12	28.0	29.8
9	24	1	28.6	26.0
9	24	2	20.8	-22.4
9	24	3	11.8	-10.9
9	24	4	23.8	22.2
9	24	5	18.8	15.9
9	24	6	18.7	-15.9
9	24	7	23.8	22.2
9	24	8	13.5	-12.0
9	24	9	20.9	-19.1
9	24	10	15.2	12.9
9	25	1	33.6	30.4
9	25	2	15.9	-17.4
9	25	3	20.0	14.8
9	25	4	30.4	28.5
9	25	5	54.9	-54.2
9	25	6	37.0	34.2
9	25	7	13.7	-13.1
9	25	8	16.8	19.2
9	25	9	47.3	-52.1
9	25	10	52.2	54.6
9	26	1	22.7	19.2
9	26	2	19.3	23.4
9	26	3	49.7	-42.4
9	26	4	15.8	13.9
9	26	5	43.2	41.3
9	26	6	21.2	-18.9
9	26	7	12.2	11.8
9	26	8	24.3	-27.0
9	26	9	24.1	21.7
9	26	10	20.3	-18.6
9	26	11	25.6	-18.1
9	26	12	28.0	29.8
9	27	1	28.6	26.0
9	27	2	20.8	-22.4
9	27	3	11.8	-10.9
9	27	4	23.8	22.2
9	27	5	18.8	15.9
9	27	6	18.7	-15.9
9	27	7	23.8	22.2
9	27	8	13.5	-12.0
9	27	9	20.9	-19.1
9	27	10	15.2	12.9
9	28	1	33.6	30.4
9	28	2	15.9	-17.4
9	28	3	20.0	14.8
9	28	4	30.4	28.5
9	28	5	54.9	-54.2
9	28	6	37.0	34.2
9	28	7	13.7	-13.1
9	28	8	16.8	19.2
9	28	9	47.3	-52.1
9	28	10	52.2	54.6
9	29	1	22.7	19.2
9	29	2	19.3	23.4
9	29	3	49.7	-42.4
9	29	4	15.8	13.9
9	29	5	43.2	41.3
9	29	6	21.2	-18.9
9	29	7	12.2	11.8
9	29	8	24.3	-27.0
9	29	9	24.1	21.7
9	29	10	20.3	-18.6
9	29	11	25.6	-18.1
9	29	12	28.0	29.8
9	30	1	28.6	26.0
9	30	2	20.8	-22.4
9	30	3	11.8	-10.9
9	30	4	23.8	22.2
9	30	5	18.8	15.9
9	30	6	18.7	-15.9
9	30	7	23.8	22.2
9	30	8	13.5	-12.0
9	30	9	20.9	-19.1
9	30	10	15.2	12.9
9	31	1	33.6	30.4
9	31	2	15.9	-17.4
9	31	3	20.0	14.8
9	31	4	30.4	28.5
9	31	5	54.9	-54.2
9	31	6	37.0	34.2
9	31	7	13.7	-13.1
9	31	8	16.8	19.2
9	31	9	47.3	-52.1
9	31	10	52.2	54.6
9	32	1	22.7	19.2
9	32	2	19.3	23.4
9	32	3	49.7	-42.4
9	32	4	15.8	13.9
9	32	5	43.2	41.3
9	32	6	21.2	-18.9
9	32	7	12.2	11.8
9	32	8	24.3	-27.0
9	32	9	24.1	21.7
9	32	10	20.3	-18.6
9	32	11	25.6	-18.1
9	32	12	28.0	29.8
9	33	1	28.6	26.0
9	33	2	20.8	-22.4
9	33	3	11.8	-10.9
9	33	4	23.8	22.2
9	33	5	18.8	15.9
9	33	6	18.7	-15.9
9	33	7	23.8	22.2
9	33	8	13.5	-12.0
9	33	9	20.9	-19.1
9	33	10	15.2	12.9
9	34	1	33.6	30.4
9	34	2	15.9	-17.4
9	34	3	20.0	14.8
9	34	4	30.4	28.5
9	34	5	54.9	-54.2
9	34	6	37.0	34.2
9	34	7	13.7	-13.1
9	34	8	16.8	19.2
9	34	9	47.3	-52.1
9	34	10	52.2	54.6
9	35	1	22.7	19.2
9	35	2	19.3	23.4
9	35	3	49.7	-42.4
9	35	4	15.8	13.9
9	35	5	43.2	41.3
9	35	6	21.2	-18.9
9	35	7	12.2	11.8
9	35	8	24.3	-27.0
9	35	9	24.1	21.7
9	35	10	20.3	-18.6
9	35	11	25.6	-18.1
9	35	12	28.0	29.8
9	36	1	28.6	26.0
9	36	2	20.8	-22.4
9	36	3	11.8	-10.9
9	36	4	23.8	22.2
9	36	5	18.8	15.9
9	36	6	18.7	-15.9
9	36	7	23.8	22.2
9	36	8	13.5	-12.0
9	36	9	20.9	-19.1
9	36	10	15.2	12.9
9	37	1	33.6	30.4
9	37	2	15.9	-17.4
9	37	3	20.0	14.8
9	37	4	30.4	28.5
9	37	5	54.9	-54.2
9	37	6	37.0	34.2
9	37	7	13.7	-13.1
9	37	8	16.8	19.2
9	37	9	47.3	-52.1
9	37	10	52.2	54.6
9	38	1	22.7	19.2
9	38	2	19.3	23.4
9	38	3	49.7	-42.4
9	38	4	15.8	13.9
9	38	5	43.2	41.3
9	38	6	21.2	-18.9
9	38	7	12.2	11.8
9	38	8	24.3	-27.0
9	38	9	24.1	21.7
9	38	10	20.3	-18.6
9	38	11	25.6	-18.1
9	38	12	28.0	29.8
9	39	1	28.6	26.0
9	39	2	20.8	-22.4
9	39	3	11.8	-10.9
9	39	4	23.8	22.2
9	39	5	18.8	15.9
9	39	6	18.7	-15.9
9	39	7	23.8	22.2
9	39	8	13.5	-12.0
9	39	9	20.9	-19.1
9	39	10	15.2	12.9
9	40	1	33.6	30.4
9	40	2	15.9	-17.4
9	40	3	20.0	14.8
9	40	4	30.4	28.5
9	40	5	54.9	-54.2
9	40	6	37.0	34.2
9	40	7	13.7	-13.1
9	40	8	16.8	19.2
9	40	9	47.3	-52.1
9	40	10	52.2	54.6
9	41	1	22.7	19.2
9	41	2	19.3	23.4
9	41	3	49.7	-42.4
9	41	4	15.8	13.9
9	41	5	43.2	41.3
9	41	6	21.2	-18.9
9	41	7	12.2	11.8
9	41	8	24.3	-27.0
9	41	9	24.1	21.7
9	41	10	20.3	-18.6
9	41	11	25.6	-18.1
9	41	12	28.0	29.8
9	42	1	28.6	26.0
9	42	2	20.8	-22.4
9	42	3	11.8	-10.9
9	42	4	23.8	22.2
9	42	5	18.8	15.9
9	42	6	18.7	-15.9
9	42	7	23.8	22.2
9	42	8	13.5	-12.0
9	42	9	20.9	-19.1
9	42	10	15.2	12.9
9	43	1	33.6	30.4
9	43	2	15.9	-17.4
9	43	3	20.0	14.8
9	43	4	30.4	28.5
9	43	5	54.9	-54.2
9	43	6	37.0	34.2
9	43	7	13.7	-13.1
9	43	8	16.8	19.2
9	43	9	47.3	-52.1
9	43	10	52.2	54.6
9	44	1	22.7	19.2
9	44	2	19.3	23.4
9	44	3	49.7	-42.4
9	44	4	15.8	13.9
9	44	5	43.2	41.3
9	44	6	21.2	-18.9
9	44	7	12.2	11.8
9	44	8	24.3	-

H	K	L	F OBS	F CALC
4	7	5	31.3	-33.0
4	7	4	37.9	37.0
4	7	3	96.2	94.4
4	7	2	39.1	-41.3
4	7	1	35.2	-39.3
4	7	0	46.2	46.5
4	6	21	33.6	-32.0
4	6	20	41.0	37.4
4	6	19	41.6	39.1
4	6	18	42.5	41.4
4	6	17	38.1	37.4
4	6	16	42.6	41.4
4	6	15	91.3	92.3
4	6	14	37.7	37.4
4	6	13	39.6	39.2
4	6	12	44.2	43.7
4	6	11	47.8	48.0
4	6	10	42.3	41.4
4	6	9	94.2	94.1
4	6	8	42.7	42.6
4	6	7	98.6	96.3
4	6	6	47.2	45.0
4	6	5	92.9	89.9
4	6	4	44.1	43.5
4	6	3	90.3	91.2
4	6	2	42.1	40.5
4	6	1	93.3	93.6
4	6	0	44.5	44.2
4	5	21	33.6	-33.9
4	5	20	41.1	39.2
4	5	19	94.3	95.6
4	5	18	39.3	39.6
4	5	17	39.6	42.1
4	5	16	39.2	44.3
4	5	15	48.4	49.2
4	5	14	46.6	48.2
4	5	13	46.6	48.2
4	5	12	40.6	39.5
4	5	11	45.9	49.6
4	5	10	47.5	47.5
4	5	9	45.0	43.5
4	5	8	48.1	48.2
4	5	7	77.2	81.3
4	5	6	41.2	45.9
4	5	5	96.5	91.2
4	5	4	39.5	39.6
4	5	3	91.2	91.2
4	5	2	38.5	37.4
4	5	1	23.3	24.0
4	5	0	32.4	33.6
4	4	23	26.4	27.9
4	4	22	31.2	30.9
4	4	21	36.9	36.0
4	4	20	39.6	39.2
4	4	19	45.5	45.0
4	4	18	41.1	41.4
4	4	17	39.6	39.2
4	4	16	42.6	42.6
4	4	15	39.6	39.2
4	4	14	36.7	36.0
4	4	13	39.6	39.2
4	4	12	39.6	39.2
4	4	11	39.6	39.2
4	4	10	39.6	39.2
4	4	9	39.6	39.2
4	4	8	39.6	39.2
4	4	7	39.6	39.2
4	4	6	39.6	39.2
4	4	5	39.6	39.2
4	4	4	39.6	39.2
4	4	3	39.6	39.2
4	4	2	39.6	39.2
4	4	1	39.6	39.2
4	4	0	39.6	39.2
4	3	25	39.6	39.2
4	3	24	39.6	39.2
4	3	23	39.6	39.2
4	3	22	39.6	39.2
4	3	21	39.6	39.2
4	3	20	39.6	39.2
4	3	19	39.6	39.2
4	3	18	39.6	39.2
4	3	17	39.6	39.2
4	3	16	39.6	39.2
4	3	15	39.6	39.2
4	3	14	39.6	39.2
4	3	13	39.6	39.2
4	3	12	39.6	39.2
4	3	11	39.6	39.2
4	3	10	39.6	39.2
4	3	9	39.6	39.2
4	3	8	39.6	39.2
4	3	7	39.6	39.2
4	3	6	39.6	39.2
4	3	5	39.6	39.2
4	3	4	39.6	39.2
4	3	3	39.6	39.2
4	3	2	39.6	39.2
4	3	1	39.6	39.2
4	3	0	39.6	39.2
4	2	23	39.6	39.2
4	2	22	39.6	39.2
4	2	21	39.6	39.2
4	2	20	39.6	39.2
4	2	19	39.6	39.2
4	2	18	39.6	39.2
4	2	17	39.6	39.2
4	2	16	39.6	39.2
4	2	15	39.6	39.2
4	2	14	39.6	39.2
4	2	13	39.6	39.2
4	2	12	39.6	39.2
4	2	11	39.6	39.2
4	2	10	39.6	39.2
4	2	9	39.6	39.2
4	2	8	39.6	39.2
4	2	7	39.6	39.2
4	2	6	39.6	39.2
4	2	5	39.6	39.2
4	2	4	39.6	39.2
4	2	3	39.6	39.2
4	2	2	39.6	39.2
4	2	1	39.6	39.2
4	2	0	39.6	39.2
4	1	26	39.6	39.2
4	1	25	39.6	39.2
4	1	24	39.6	39.2
4	1	23	39.6	39.2
4	1	22	39.6	39.2
4	1	21	39.6	39.2
4	1	20	39.6	39.2
4	1	19	39.6	39.2
4	1	18	39.6	39.2
4	1	17	39.6	39.2
4	1	16	39.6	39.2
4	1	15	39.6	39.2
4	1	14	39.6	39.2
4	1	13	39.6	39.2
4	1	12	39.6	39.2
4	1	11	39.6	39.2
4	1	10	39.6	39.2
4	1	9	39.6	39.2
4	1	8	39.6	39.2
4	1	7	39.6	39.2
4	1	6	39.6	39.2
4	1	5	39.6	39.2
4	1	4	39.6	39.2
4	1	3	39.6	39.2
4	1	2	39.6	39.2
4	1	1	39.6	39.2
4	1	0	39.6	39.2
4	0	24	39.6	39.2
4	0	23	39.6	39.2
4	0	22	39.6	39.2
4	0	21	39.6	39.2
4	0	20	39.6	39.2
4	0	19	39.6	39.2
4	0	18	39.6	39.2
4	0	17	39.6	39.2
4	0	16	39.6	39.2
4	0	15	39.6	39.2
4	0	14	39.6	39.2
4	0	13	39.6	39.2
4	0	12	39.6	39.2
4	0	11	39.6	39.2
4	0	10	39.6	39.2
4	0	9	39.6	39.2
4	0	8	39.6	39.2
4	0	7	39.6	39.2
4	0	6	39.6	39.2
4	0	5	39.6	39.2
4	0	4	39.6	39.2
4	0	3	39.6	39.2
4	0	2	39.6	39.2
4	0	1	39.6	39.2
4	0	0	39.6	39.2

H	K	L	F OBS	F CALC
3	3	2	9.3	-10.9
3	3	1	31.2	23.5
3	3	0	12.0	-20.8
3	2	24	9.7	-7.6
3	2	23	23.3	-23.8
3	2	22	29.3	29.3
3	2	21	42.6	41.8
3	2	20	32.7	-32.0
3	2	19	12.2	-15.1
3	2	18	32.5	29.6
3	2	17	45.2	47.8
3	2	16	47.1	-45.7
3	2	15	34.9	-36.0
3	2	14	48.9	-48.3
3	2	13	49.3	45.1
3	2	12	34.7	-35.7
3	2	11	49.3	45.1
3	2	10	34.7	-35.7
3	2	9	125.5	116.4
3	2	8	55.8	53.0
3	2	7	83.6	-84.4
3	2	6	16.9	-15.1
3	2	5	94.2	81.9
3	2	4	45.3	49.9
3	2	3	99.5	-97.6
3	2	2	17.5	-16.0
3	2	1	132.5	117.3
3	2	0	121.1	-133.2
3	1	27	31.4	29.3
3	1	26	27.1	-29.2
3	1	25	9.7	-11.0
3	1	24	12.1	-9.2
3	1	23	44.6	42.1
3	1	22	113.3	94.5
3	1	21	27.6	-29.3
3	1	20	12.0	8.8
3	1	19	83.5	-83.9
3	1	18	45.3	40.9
3	1	17	9.1	8.7
3	1	16	60.2	64.7
3	1	15	37.3	29.8
3	1	14	19.5	18.0
3	1	13	125.1	-126.3
3	1	12	52.1	-53.0
3	1	11	101.5	92.1
3	1	10	8.6	-4.2
3	1	9	47.9	-53.3
3	1	8	8.9	11.0
3	1	7	70.5	-74.1
3	1	6	46.2	-38.8
3	1	5	76.9	64.0
3	1	4	83.7	76.9
3	1	3	8.1	-15.7
3	1	2	62.4	-78.8
3	1	1	15.3	-23.5
3	1	0	34.2	-30.4
3	0	24	31.4	31.5
3	0	18	92.9	90.7
3	0	16	68.3	-67.3
3	0	14	40.5	42.5
3	0	12	45.7	49.4
3	0	10	53.2	-57.6
3	0	8	166.4	149.9
3	0	6	68.2	-62.2
3	0	4	78.8	-80.3
3	0	2	241.0	255.5
3	0	0	241.0	-266.9
2	2	25	18.8	-19.3
2	2	24	12.1	-12.6
2	2	23	19.4	22.1
2	2	22	44.7	45.9
2	2	21	19.5	-17.2
2	2	20	24.0	-24.2
2	2	19	44.5	44.5
2	2	18	80.5	81.5
2	2	17	97.0	87.3
2	2	16	132.4	-108.9
2	2	15	99.3	-90.3
2	2	14	89.6	89.6
2	2	13	94.4	91.1
2	2	12	84.7	-81.1
2	2	11	82.4	87.6
2	2	10	77.3	-75.3
2	2	9	119.1	-113.7
2	2	8	29.3	-23.6
2	2	7	11.9	11.6
2	2	6	11.4	-18.8
2	2	5	22.8	-23.6
2	2	4	33.4	34.1
2	2	3	15.3	23.3
2	2	2	11.9	-8.7
2	2	1	32.0	-38.4
2	2	0	14.3	14.6
2	1	27	42.6	41.8
2	1	26	29.4	-29.2
2	1	25	9.4	-11.0
2	1	24	10.5	10.2
2	1	23	34.5	-34.9
2	1	22	11.9	15.0
2	1	21	40.9	41.1
2	1	20	19.2	-17.5
2	1	19	43.2	-45.2
2	1	18	31.5	29.2
2	1	17	32.5	-34.9
2	1	16	92.7	92.7
2	1	15	43.4	-44.1
2	1	14	19.3	-23.8
2	1	13	95.0	-115.5
2	1	12	49.1	-23.8
2	1	11	34.4	-33.4
2	1	10	91.4	92.2
2	1	9	9.7	10.0
2	1	8	33.8	-35.4
2	1	7	77.0	77.6
2	1	6	34.7	36.6
2	1	5	42.1	41.0
2	1	4	144.0	130.3
2	1	3	32.5	-34.9
2	1	2	95.0	-115.5
2	1	1	49.1	-23.8
2	1	0	34.4	-33.4
2	0	24	31.4	32.2
2	0	22	9.7	10.0
2	0	20	44.6	-43.1
2	0	18	77.0	77.6
2	0	16	49.5	-23.2
2	0	14	102.1	95.6
2	0	12	79.5	-75.8
2	0	10	99.2	99.5
2	0	8	21.4	-21.6
2	0	6	199.1	-174.6
2	0	4	195.0	15.1
2	0	2	95.1	23.7
2	0	0	40.8	19.0
1	10	4	40.8	19.0
1	10	2	12.8	-21.6
1	10	0	12.8	-21.6
1	9	13	15.9	15.6
1	9	11	17.3	17.1
1	9	9	45.2	-37.2
1	9	7	49.8	26.9
1	9	5	49.2	-42.4
1	9	3	45.2	43.4
1	9	1	49.2	43.4
1	8	15	13.5	13.4
1	8	14	42.9	22.0
1	8	12	13.5	-10.5
1	8	12	45.2	-35.2
1	8	10	13.4	12.0
1	8	8	19.3	14.9

H	K	L	F OBS	F CALC
1	8	7	10.1	-10.5
1	8	6	29.0	-27.6
1	8	5	24.0	23.7
1	8	4	28.9	29.7
1	8	3	25.6	-28.1
1	8	0	28.1	-31.7
1	7	24	10.6	11.9
1	7	17	33.7	34.9
1	7	16	38.2	-38.9
1	7	15	12.2	-10.5
1	7	14	12.3	13.2
1	7	11	23.5	22.9
1	7	10	42.1	-44.7
1	7	9	45.8	-44.1
1	7	8	46.6	46.9
1	7	7	49.6	48.3
1	7	5	12.6	-12.6
1	7	4	28.7	-30.9
1	7	3	39.9	-37.1
1	7	2	54.4	57.9
1	7	1	52.9	52.6
1	7	0	37.4	-36.9
1	6	23	35.1	34.2
1	6	21	24.3	-23.9
1	6	12	12.3	13.2
1	6	11	23.5	22.9
1	6	10	42.1	-44.7
1	6	9	45.8	-44.1
1	6	8	46.6	46.9
1	6	7	49.6	48.3
1	6	5	12.6	-12.6
1	6	4	28.7	-30.9
1	6	3	39.9	-37.1
1	6	2	54.4	57.9
1	6	1	52.9	52.6
1	6	0	37.4	-36.9
1	5	24	30.1	30.9
1	5	23	9.3	-9.7
1	5	22	34.0	-34.5
1	5	19	12.4	12.6
1	5	18	38.5	41.0
1	5	16	78.6	-79.1
1	5	15	10.8	-8.5
1	5	14	54.9	56.5
1	5	13	14.9	-11.6
1	5	12	14.6	12.4
1	5	11	27.7	28.1
1	5	10	65.9	-66.9
1	5	9	11.9	-14.2
1	5	8	57.4	53.1
1	5	7	17.4	-18.9
1	5	6	9.9	-9.3
1	5	5	19.6	-18.6
1	5	4	51.5	-50.9
1	5	3	11.6	-15.2
1	5	2	98.8	92.4
1	5	1	44.5	44.5
1	5	0	74.3	-77.4
1	4	25	25.4	-25.3
1	4	23	11.7	-9.8
1	4	21	37.1	37.2
1	4	20	24.0	-24.2
1	4	19	65.5	-67.9
1	4	18	11.9	-8.7
1	4	15	32.0	35.4
1	4	14	14.4	-11.4
1	4	13	74.1	-73.9
1	4	11	62.0	61.7
1	4	10	13.7	-10.4
1	4	9	18.1	18.7
1	4	7	60.3	-56.1
1	4	6	33.1	29.4
1	4	5	141.4	132.8
1	4	4	36.7	-35.9
1	4	3	38.3	-41.0
1	4	2	98.7	93.1
1	4	1	70.9	-70.9
1	4	0	7.5	-5.7
1	3	24	38.1	39.3
1	3	23	12.9	-13.2
1	3	22	51.1	-54.3
1	3	21	37.0	36.3
1	3	20	16.3	17.2
1	3	19	14.7	13.0
1	3	18	46.5	47.1
1	3	16	44.0	-44.5
1	3	15	49.8	51.2
1	3	14	49.2	50.3
1	3	13	18.4	17.1
1	3	11	85.3	-75.1
1	3	10	96.0	-91.0
1	3	9	82.8	84.1
1	3	8	87.7	90.5
1	3	7	70.4	-17.0
1	3	6	28.9	-19.9
1	3	5	72.1	-72.4
1	3	4	42.1	-41.3
1	3	3	121.0	-105.8
1	3	2	72.4	64.0
1	3	1	134.9	131.3
1	3	0	27.0	-27.4
1	2	25	20.9	23.2
1	2	24	24.7	-25.0
1	2	23	17.0	-17.9
1	2	22	15.2	15.2
1	2	21	48.6	44.8
1	2	20	49.7	-49.6
1	2	19	59.0	-59.0
1	2	18	34.8	33.0
1	2	17	36.6	36.5
1	2	16	34.9	-31.6
1	2	14	11.4	-10.9
1	2	13	44.2	-49.4
1	2	12	91.9	88.6
1	2	10	94.6	-83.6
1	2	9	10.4	3.2
1	2	7	63.5	-49.1
1	2	6	82.2	84.2
1	2	5	47.9	45.0

H	K	L	F OBS	F CALC
1	2	4	45.4	-39.3
1	2	3	43.8	-44.9
1	2	2	66.2	-53.9
1	2	1	23.0	-17.4
1	2	0	62.2	75.0
1	1	26	15.1	-12.1
1	1	25	32.2	32.0
1	1	24	18.4	16.3
1	1	23	33.3	-32.9
1	1	22	19.5	-19.6
1	1	21	22.2	22.5
1	1	20	19.8	18.6
1	1	19	23.0	21.5
1	1	18	65.8	-67.2
1	1	17	39.3	-32.8
1	1	15	79.5	78.2
1	1	14	24.8	27.1
1	1	13	9.9	-13.0
1	1	12	32.8	-28.8
1	1	11	26.7	-29.9
1	1	10	115.2	-98.2
1	1	9	95.6	100.4
1	1	8	59.1	102.2
1	1	7	98.0	-91.0
1	1	6	63.4	-71.2
1	1	5	46.8	-44.8
1	1	2	96.9	109.2
1	1	1	206.0	-177.0
1	1	0	32.7	-31.0
1	0	28	35.9	35.2
1	0	26	43.7	-41.9
1	0	24	15.3	12.1
1	0	22	27.8	29.4
1	0	20	69.6	-74.2
1	0	19	79.0	74.6
1	0	18	13.5	-14.9
1	0	16	97.9	-101.2
1	0	14	92.7	92.7
1	0	12	93.4	-98.1
1	0	10	91.0	-98.1
1	0	8	28.4	33.1
1	0	6	34.4	34.8
1	0	4	11.7	12.0
1	0	0	20.4	-23.0
0	9	13	14.2	-13.1
0	9	11	29.1	30.6
0	9	10	31.7	-29.2
0	9	9	95.6	94.9
0	9	8	12.3	-13.2
0	9	6	44.4	-46.3
0	9	5	26.3	29.0
0	9	3	13.7	-14.5
0	9	2	59.1	49.8
0	9	1	19.1	-21.0
0	9	0	70.0	-80.3
0	8	20	16.0	-14.3
0	8	19	26.3	-24.7
0	8	17	23.9	24.5
0	8	16	32.0	31.9
0	8	14	23.7	-22.0
0	8	13	29.1	-29.5
0	8	12	23.0	-18.5
0	8	11	41.7	43.8
0	8	10	45.4	43.9
0	8	9	10.1	-29.5
0	8	8	51.9	-44.3
0	8	7	21.6	-19.9
0	8	6	12.5	10.9
0	8	5	43.0	44.8
0	8	4	50.0	49.5
0	8	3	35.9	-35.9
0	8	2	79.8	-79.4
0	8	1	19.6	19.6
0	8	0	29.7	29.7
0	7	21	28.1	29.4
0	7	20	20.7	20.2
0	7	18	17.0	-15.9
0	7	17	19.7	19.9
0	7	16	20.1	-19.9
0	7	15	40.5	42.6
0	7	14	24.1	24.4
0	7	13	19.6	-18.0
0	7	11	9.8	9.0
0	7	10	35.4	-33.8
0	7	9	49.6	49.4
0	7	8	48.3	54.3
0	7	7	79.9	-77.7
0	7	6	27.1	-26.0
0	7	5	31.6	30.7
0	7	4	8.0	10.4
0	7	3	22.9	23.3
0	7	2	36.6	35.7
0	7	1	95.7	-93.8
0	7	0	34.9	-29.8
0	6	24	28.2	28.4
0	6	20	35.3	-37.1
0	6	18	58.2	55.9
0	6	17	10.6	17.9
0	6	16	26.4	-29.1
0	6	14	33.3	-32.1
0	6	13	18.3	19.8
0	6	12	76.4	75.0
0	6	11	13.9	18.4
0	6	10	67.1	-65.7
0	6	9	20.5	-19.4
0	6	8	42.2	39.2
0	6	5	38.1	-29.4
0	6	4	90.4	-91.4
0	6	3	33.2	-32.0
0	6	2	74.7	79.6
0	6	1	38.3	-31.7
0	6	0	38.3	34.9
0	5	24	22.8	24.2
0	5	20	35.3	-37.1
0	5	18	54.2	55.9
0	5	17	10.6	17.9
0	5	16	26.4	-29.1
0	5	14	33.3	-32.1
0	5	13	18.3	19.8
0	5	12	76.4	75.0
0	5	11	13.9	18.4
0	5	10	67.1	-65.7
0	5	7	20.5	-19.4
0	5	6	42.2	39.2
0	5	5	38.1	-29.4
0	5	4	90.4	-91.4
0	5	3	33.2	-32.0
0	5	2	74.7	79.6
0	4	23	38.3	-31.7
0	4	22	16.7	15.9
0	4	21	38.0	34.9
0	4	20	20.6	-19.6
0	4	19	33.1	-31.1
0	4	18	36.7	-35.0
0	4	16	11.6	11.0
0	4	15	74.3	73.0
0	4	14	12.6	-13.3
0	4	13	55.4	-59.8
0	4	12	30.1	26.7
0	4	9	40.1	72.6

H	K	L	F OBS	F CALC
0	4	7	97.7	-94.2
0	4	6	72.5	32.3
0	4	5	74.2	69.4
0	4	3	79.1	72.8
0	4	2	9.1	15.4
0	4	1	195.8	-181.5
0	4	0	7.5	5.3
0	3	27	14.0	-17.7
0	3	26	47.7	-24.1
0	3	25	70.9	22.5
0	3	24	48.4	2.3
0	3	23	14.5	21.1
0	3	20	46.1	-41.0
0	3	19	47.1	36.3
0	3	18	95.6	55.2
0	3	17	18.7	-27.8
0	3	16	140.7	-145.6
0	3	15	91.9	83.7
0	3	12	119.2	117.2
0	3	1	72.1	-63.6
0	2	27	12.3	15.3
0	2	26	18.6	-17.0
0	2	25	13.4	14.5
0	2	24	42.4	-21.5
0	2	23	48.7	-44.3
0	2	22	72.5	53.4
0	2	21	90.7	83.0
0	2	20	41.3	24.3
0	2	19	16.9	15.5
0	2	17	46.5	34.9
0	2	16	145.2	134.5
0	2	15	17.9	-27.9
0	2	10	46.1	37.7
0	2	9	149.3	97.6
0	2	8	137.6	-143.4
0	2	7	76.9	-115.1
0	2	6	145.3	113.5
0	2	5	46.2	3.7
0	2	4	44.5	27.1
0	2	3	93.7	31.5
0	2	2	90.5	-135.8
0	2	1	47.4	-50.5
0	2	0	140.3	111.7
0	1	27	47.4	25.9
0	1	25	58.6	44.9
0	1	23	70.5	27.4
0	1	21	46.1	25.9
0	1	20	41.3	-17.6
0	1	19	99.9	77.6
0	1	17	140.3	-116.4
0	1	16	18.4	29.5
0	1	15	42.8	32.1
0	1	14	96.4	57.5
0	1	13	140.1	112.4
0	1	12	7.4	6.9
0	1	11	134.3	-134.6
0	1	10	48.4	-40.5
0	1	9	14.6	12.4
0	1	8	4.1	-9.6
0	1	7	85.2	52.6
0	1	6	156.9	127.3
0	1	5	148.7	-161.1
0	1	4	115.6	-130.4
0	1	3	141.4	108.1
0	1	2	34.4	15.3
0	1	1	105.8	-156.8
0	0	28	49.0	24.8
0	0	26	11.9	-12.5
0	0	24	17.1	-17.9
0	0	22	30.5	34.3
0	0	20	45.9	-23.1
0	0	18	75.3	59.5
0	0	16	190.0	-191.2
0	0	12	43.1	19.6
0	0	10	48.5	34.3
0	0	8	190.0	-189.8
1	0	4	49.6	-27.1
1	0	2	36.9	37.6
1	0	1	12.9	4.9
1	0	0	119.2	117.2
1	1	27	30.5	22.5
1	1	26	47.7	44.6
1	1	25	42.3	27.6
1	1	24	19.4	19.5
1	1	23	36.6	14.9
1	1	22	31.2	34.6
1	1	21	40.1	44.6
1	1	20	28.6	27.2
1	1	19	49.9	50.0
1	1	18	10.5	10.2
1	1	17	30.3	31.9
1	1	15	78.2	77.0
1	1	14	14.0	13.0
1	1	13	118.4	112.4
1	1	12	38.8	25.2
1	1	11	43.1	35.0
1	1	10	14.0	19.2
1	1	9	87.6	75.5
1	1	7	113.6	126.8
1	0	26	27.8	30.2
1	0	24	27.5	30.2
1	0	22	14.6	11.8
1	0	20	26.1	24.1
1	0	18	56.0	54.9
1	0	16	89.4	86.7
1	0	14	19.1	19.3
1	0	12	116.2	109.3
1	0	10	134.0	137.4
1	0	8	107.6	90.6
2	10	2	15.0	15.4
2	9	11	9.9	4.5
H	K	L	F OBS	F CALC
-1	7	2	13.8	13.6
-1	7	1	35.6	-34.9
-1	6	19	22.4	22.0
-1	6	18	20.3	20.7
-1	6	17	31.3	-28.4
-1	6	16	26.1	-29.5
-1	6	15	26.0	23.7
-1	6	14	9.8	8.8
-1	6	12	29.5	26.6
-1	6	11	28.7	-26.1
-1	6	10	43.7	-42.5
-1	6	9	66.9	62.9
-1	6	8	42.7	39.6
-1	6	7	46.0	-46.9
-1	6	6	20.8	-21.5
-1	6	5	22.7	-21.0
-1	6	3	70.2	66.5
-1	6	2	35.1	34.1
-1	6	1	94.0	-82.3
-1	5	22	25.2	25.6
-1	5	20	44.1	-42.3
-1	5	19	17.0	-13.6
-1	5	18	34.7	35.3
-1	5	16	17.3	15.0
-1	5	14	17.2	-13.9
-1	5	13	15.3	-15.3
-1	5	12	86.4	85.5
-1	5	10	30.1	-31.7
-1	5	8	51.0	-50.7
-1	5	7	19.5	-25.7
-1	5	6	99.6	84.0
-1	5	5	14.0	9.1
-1	5	4	60.1	-59.6
-1	5	2	11.7	-10.2
-1	5	1	11.0	-14.7
-1	4	25	17.8	19.7
-1	4	24	9.6	-5.5
-1	4	23	33.9	-36.1
-1	4	22	18.1	19.1
-1	4	19	23.4	23.1
-1	4	18	11.2	-12.3
-1	4	17	67.5	-65.1
-1	4	16	16.9	19.7
-1	4	15	47.2	47.9
-1	4	13	12.6	15.5
-1	4	11	99.9	-87.5
-1	4	10	25.1	23.9
-1	4	9	92.0	90.3
-1	4	8	18.5	-14.6
-1	4	7	75.9	-65.9
-1	4	6	14.0	9.4
-1	4	5	9.9	2.6
-1	4	4	32.7	33.0
-1	4	3	156.8	148.8
-1	4	2	74.7	-32.3
-1	4	1	183.1	-179.5
-1	3	26	12.8	-15.7
-1	3	22	30.3	29.4
-1	3	21	33.6	-33.3
-1	3	20	54.5	-56.4
-1	3	19	21.5	22.4
-1	3	18	23.3	23.9
-1	3	16	19.3	24.1
-1	3	15	44.2	-37.1
-1	3	14	56.8	-49.7
-1	3	13	27.7	31.6
-1	3	12	90.2	91.7
-1	3	11	30.5	-27.0
-1	3	10	42.4	-31.1
-1	3	9	47.7	-41.0
-1	3	8	51.4	-49.2
-1	3	7	127.6	119.5
-1	3	6	154.6	153.6
-1	3	5	93.2	-89.0
-1	3	4	119.5	-107.3
-1	3	3	58.3	45.8
-1	3	1	38.2	24.8
-1	2	24	23.4	23.5
-1	2	23	12.6	10.2
-1	2	22	19.1	-39.6
-1	2	21	37.4	39.1
-1	2	20	45.1	44.0
-1	2	19	24.9	24.3
-1	2	18	45.2	45.6
-1	2	17	30.8	-29.7
-1	2	16	49.4	53.9
-1	2	15	30.0	34.0
-1	2	13	30.8	-19.3
-1	2	12	48.9	-38.6
-1	2	11	92.8	-86.4
-1	2	10	112.3	113.6
-1	2	9	106.6	115.7
-1	2	8	38.1	43.9
-1	2	6	29.3	44.0
-1	2	3	170.3	112.0
-1	2	2	215.5	-191.5
-1	2	1	30.7	32.2
-1	1	27	39.5	-40.2
-1	1	25	25.5	24.4
-1	1	22	12.9	13.9
-1	1	21	40.1	-43.6
-1	1	20	28.6	-27.2
-1	1	19	49.9	50.0
-1	1	18	10.5	-10.2
-1	1	17	30.3	-31.9
-1	1	15	78.2	-77.0
-1	1	14	14.0	-13.0
-1	1	13	118.4	112.4
-1	1	12	38.8	-25.2
-1	1	11	43.1	-35.0
-1	1	10	14.0	19.2
-1	1	9	87.6	-75.5
-1	1	7	113.6	126.8
-1	0	26	27.8	30.2
-1	0	24	27.5	-30.2
-1	0	22	14.6	11.8
-1	0	20	26.1	24.1
-1	0	18	56.0	-54.9
-1	0	16	89.4	86.7
-1	0	14	19.1	-19.3
-1	0	12	116.2	-109.3
-1	0	10	134.0	137.4
-1	0	8	107.6	-90.6
2	10	2	15.0	15.4
2	9	11	9.9	4.5
H	K	L	F OBS	F CALC
-2	9	9	25.0	21.1
-2	9	7	34.7	-36.7
-2	9	5	31.4	30.7
-2	9	3	27.9	26.6
-2	9	2	11.8	10.2
-2	9	1	38.9	-41.8
-2	8	17	11.9	-13.9
-2	8	16	10.7	-9.6
-2	8	15	9.5	5.6
-2	8	14	11.9	-9.9
-2	8	13	10.9	19.1
-2	8	12	36.4	36.8
-2	8	11	12.4	-15.2
-2	8	10	33.5	-32.3
-2	8	8	11.6	7.2
-2	8	7	11.0	8.7
-2	8	6	12.5	12.6
-2	8	5	9.6	-8.6
-2	8	4	43.1	-43.0
-2	8	3	14.2	14.2
-2	8	2	12.2	11.1
-2	8	1	15.6	-17.5
-2	7	17	18.7	-19.9
-2	7	16	23.9	23.5
-2	7	15	23.8	24.5
-2	7	14	29.6	-30.9
-2	7	13	18.5	-15.8
-2	7	11	20.8	-19.8
-2	7	10	28.2	29.0
-2	7	9	52.8	54.1
-2	7	8	48.0	-47.0
-2	7	7	46.4	-45.7
-2	7	6	19.0	19.7
-2	7	5	27.4	25.9
-2	7	3	14.1	12.9
-2	7	2	23.0	-25.7
-2	6	21	29.8	-30.0
-2	6	20	19.2	-19.0
-2	6	19	38.0	35.8
-2	6	18	21.9	21.3
-2	6	17	31.0	-28.3
-2	6	16	21.6	-19.8
-2	6	13	36.1	33.1
-2	6	12	23.7	28.4
-2	6	11	60.2	-58.4
-2	6	10	33.0	-32.3
-2	6	9	52.2	54.8
-2	6	8	10.4	8.7
-2	6	5	65.3	-68.3
-2	6	4	14.0	-15.5
-2	6	3	89.9	70.9
-2	6	2	11.6	14.5
-2	6	1	13.8	-15.3
-2	5	24	19.3	-22.2
-2	5	22	34.9	35.5
-2	5	21	20.9	-23.8
-2	5	18	16.2	-16.1
-2	5	17	10.5	-8.9
-2	5	16	49.2	44.2
-2	5	14	74.5	-73.8
-2	5	13	23.9	20.3
-2	5	12	29.2	27.1
-2	5	11	22.3	-22.3
-2	5	10	35.1	36.2
-2	5	9	11.3	13.5
-2	5	8	71.4	-70.2
-2	5	7	12.1	-9.9
-2	5	6	52.2	55.3
-2	5	5	21.4	24.1
-2	5	2	60.2	-58.2
-2	5	1	32.7	33.7
-2	4	25	19.8	17.6
-2	4	21	30.4	-27.4
-2	4	19	51.8	50.3
-2	4	17	39.8	-44.3
-2	4	13	85.3	85.0
-2	4	11	120.7	-119.9
-2	4	9	50.8	48.7
-2	4	8	29.1	-23.7
-2	4	7	43.7	43.4
-2	4	6	7.9	-3.8
-2	4	5	115.9	-112.1
-2	4	4	20.2	23.8
-2	4	3	121.6	120.9
-2	4	2	45.9	-40.3
-2	4	1	20.9	-25.9
-2	3	24	22.9	-25.2
-2	3	23	21.1	19.4
-2	3	22	43.8	42.4
-2	3	21	24.1	-25.1
-2	3	20	34.2	-34.0
-2	3	18	21.2	-21.5
-2	3	17	27.7	28.2
-2	3	16	66.1	65.0
-2	3	15	41.6	-41.4
-2	3	14	49.4	-52.0
-2	3	13	13.6	-12.6
-2	3	12	40.0	30.8
-2	3	11	51.0	46.4
-2	3	10	97.9	78.0
-2	3	9	49.2	-55.3
-2	3	8	111.2	-107.8
-2	3	7	93.3	90.5
-2	3	6	69.9	94.4
-2	3	5	30.8	-27.8
-2	3	4	49.8	34.7
-2	3	3	113.4	-107.1
-2	3	1	60.9	64.9
-2	2	27	15.0	-17.0
-2	2	26	25.2	24.7
-2	2	25	22.9	23.0
-2	2	24	19.5	-19.5
-2	2	23	21.7	-18.6
-2	2	22	61.3	-38.7
-2	2	21	54.6	54.6
-2	2	19	72.7	69.5
-2	2	18	33.9	-34.5
-2	2	17	29.0	-29.3
-2	2	16	33.4	31.8
-2	2	15	11.6	-15.1
-2	2	14	12.1	11.5
-2	2	13	37.4	29.1
-2	2	12	41.3	-38.7
-2	2	11	70.0	-71.8
-2	2	10	97.7	94.1
-2	2	9	68.7	93.0
-2	2	8	91.1	-70.2
H	K	L	F OBS	F CALC
-2	2	7	14.2	-24.3
-2	2	6	98.3	-71.4
-2	2	5	54.4	-66.1
-2	2	4	47.5	45.4
-2	2	3	119.2	100.5
-2	2	2	140.2	-124.2
-2	2	1	36.4	31.1
-2	1	27	13.9	15.3
-2	1	25	14.7	11.6
-2	1	24	12.9	11.9
-2	1	23	46.3	36.7
-2	1	22	40.2	21.1
-2	1	21	8.4	-26.3
-2	1	20	44.8	-24.9
-2	1	19	9.2	3.1
-2	1	18	41.4	-22.1
-2	1	17	48.6	46.4
-2	1	16	40.9	16.4
-2	1	15	9.2	-8.3
-2	1	14	42.7	-25.2
-2	1	13	74.6	69.5
-2	1	12	46.7	27.4
-2	1	11	134.1	-130.1
-2	1	9	70.1	-60.4
-2	1	7	149.9	124.9
-2	1	6	103.4	79.8
-2	1	5	42.5	30.9
-2	1	4	82.6	-82.0
-2	1	3	51.1	35.9
-2	1	2	144.3	-127.2
-2	1	1	183.0	171.3
-2	0	26	40.4	40.8
-2	0	24	26.6	-26.1
-2	0	22	46.5	-24.4
-2	0	20	39.4	31.3
-2	0	18	97.1	-96.4
-2	0	16	49.8	50.0
-2	0	14	31.1	47.6
-2	0	12	144.5	-137.1
-2	0	10	142.5	123.3
-2	0	8	78.1	42.9
-2	0	6	14.4	7.1
-2	0	4	143.9	101.7
-2	0	2	143.5	-163.6
-3	9	11	41.9	-19.9
-3	9	9	42.9	33.1
-3	9	7	45.4	-33.4
-3	9	3	9.8	4.7
-3	9	1	49.7	41.0
-3	8	19	40.9	31.0
-3	8	16	13.1	13.1
-3	8	15	49.3	-31.6
-3	8	13	29.5	15.4
-3	8	12	49.2	29.4
-3	8	11	10.4	-17.6
-3	8	8	47.2	-26.0
-3	8	7	15.5	17.3
-3	8	6	40.3	34.3
-3	8	5	42.7	-19.9
-3	8	4	48.4	-27.1
-3	8	3	16.3	18.2
-3	8	2	16.4	14.9
-3	7	19	17.2	17.3
-3	7	18	45.9	22.2
-3	7	17	41.5	-23.4
-3	7	16	42.1	37.4
-3	7	15	44.4	27.4
-3	7	13	13.1	-11.4
-3	7	12	26.3	-28.1
-3	7	11	49.4	-25.7
-3	7	10	42.1	37.4
-3	7	9	90.5	49.7
-3	7	8	49.2	-37.2
-3	7	7	48.6	-36.5
-3	7	6	14.3	-14.4
-3	7	5	11.0	-9.4
-3	7	4	14.8	16.5
-3	6	21	46.1	-25.9
-3	6	20	18.0	-17.9
-3	6	19	43.6	23.4
-3	6	18	17.6	14.4
-3	6	17	11.4	-12.9
-3	6	13	94.3	51.1
-3	6	12	11.7	11.4
-3	6	11	91.0	-92.6
-3	6	9	11.7	11.4
-3	6	8	42.7	-20.9
-3	6	7	96.3	95.4
-3	6	6	46.9	26.2
-3	6	5	42.4	27.2
-3	6	2	8.8	7.4
-3	6	1	93.4	97.3
-3	5	22	40.4	21.1
-3	5	21	13.0	11.4
-3	5	19	46.5	-46.1
-3	5	18	32.9	51.6
-3	5	16	24.1	27.7
-3	5	15	42.4	27.2
-3	5	14	40.4	-21.0
-3	5	13	11.7	11.3
-3	5	12	46.5	-30.3
-3	5	11	99.0	54.5
-3	5	8	41.3	-49.0
-3	5	7	17.1	-17.5
-3	5	6	45.9	17.4
-3	5	5	93.4	42.2
-3	5	3	9.4	-9.4
-3	5	2	93.4	-52.7
-3	5	1	18.0	21.5
-3	4	23	12.6	13.2
-3	4	22	15.9	16.0
-3	4	21	44.4	-43.6
-3	4	20	46.9	19.2
-3	4	19	46.7	41.4
-3	4	18	10.7	11.4
-3	4	16	43.0	32.1
-3	4	15	45.3	47.1
-3	4	14	12.6	16.1
-3	4	12	76.3	74.3
-3	4	11	11.7	10.2
H	K	L	F OBS	F CALC
-3	4	11	41.4	-42.6
-3	4	10	17.0	-18.6
-3	4	9	9.2	-12.0
-3	4	7	18.9	15.0
-3	4	6	54.6	49.1
-3	4	5	14.7	-14.6
-3	4	4	54.0	-55.9
-3	4	3	42.1	31.3
-3	4	2	19.9	13.3
-3	4	1	22.9	22.7
-3	3	26	15.5	13.8
-3	3	24	28.0	-28.2
-3	3	23	10.9	14.5
-3	3	22	24.5	22.1
-3	3	21	9.6	-8.0
-3	3	20	10.7	7.9
-3	3	19	13.8	-9.6
-3	3	18	39.7	-39.6
-3	3	17	39.6	36.7
-3	3	16	47.9	49.1
-3	3	15	37.3	-32.3
-3	3	14	27.0	-24.8
-3	3	12	11.8	-12.4
-3	3	11	46.8	44.2
-3	3	10	77.4	75.8
-3	3	9	62.8	-63.6
-3	3	8	81.3	-77.9
-3	3	7	72.6	65.6
-3	3	6	33.4	31.7
-3	3	4	75.9	68.5
-3	3	3	111.4	-118.8
-3	3	2	48.1	-49.8
-3	3	1	75.1	60.2
-3	2	27	13.4	-14.0
-3	2	26	19.8	19.8
-3	2	25	10.9	11.0
-3	2	23	17.1	17.1
-3	2	22	77.0	-26.4
-3	2	21	40.4	-42.2
-3	2	20	46.2	47.1
-3	2	19	50.9	49.7
-3	2	18	28.5	-25.6
-3	2	17	10.3	-9.9
-3	2	15	29.5	-30.0
-3	2	14	35.8	33.3
-3	2	13	32.3	31.6
-3	2	12	54.9	-52.9
-3	2	11	27.7	-28.0
-3	2	10	53.1	52.0
-3	2	8	45.5	39.1
-3	2	7	40.0	45.1
-3	2	6	105.0	-109.8
-3	2	5	66.0	-62.7
-3	2	4	57.1	47.0
-3	2	3	33.0	31.1
-3	2	2	56.8	57.7
-3	2	1	20.8	10.3
-3	1	25	37.2	-34.8
-3	1	23	45.9	46.9
-3	1	22	12.3	11.5
-3	1	20	11.6	-12.2
-3	1	19	34.7	-36.6
-3	1	18	20.3	-20.1
-3	1	17	9.8	9.1
-3	1	16	20.6	15.9
-3	1	15	69.7	-69.6
-3	1	14	13.7	-9.2
-3	1	12	20.1	-15.9
-3	1	11	86.7	82.2
-3	1	10	26.9	25.1
-3	1	9	129.4	-125.4
-3	1	8	84.5	-77.2
-3	1	7	26.7	21.5
-3	1	6	17.2	21.4
-3	1	5	19.9	14.1
-3	1	4	9.3	19.9
-3	1	3	41.3	34.5
-3	1	2	156.2	-150.7
-3	1	1	62.2	60.0
-3	0	26	29.0	28.9
-3	0	22	52.6	-50.5
-3	0	20	11.3	8.0
-3	0	18	53.8	-54.0
-3	0	16	21.0	-21.2
-3	0	14	79.1	73.2
-3	0	12	80.7	-82.7
-3	0	10	55.9	41.6
-3	0	8	76.5	73.2
-3	0	6	58.9	-66.9
-3	0	4	112.2	105.9
-3	0	2	50.8	47.0
-4	9	9	18.5	14.4
-4	9	8	32.1	-32.0
-4	9	3	34.1	32.3
-4	8	14	32.4	-29.0
-4	8	10	36.3	33.9
-4	8	9	17.3	-17.3
-4	8	5	46.7	-45.8
-4	8	4	22.0	-19.2
-4	8	3	21.2	20.8
-4	8	2	41.0	37.5
-4	8	1	11.0	9.1
-4	7	3	11.2	-10.1
-4	7	2	44.9	-45.9
-4	7	1	19.0	17.9
-4	7	15	23.4	-23.3
-4	7	13	22.0	-19.2
-4	7	12	12.8	9.1
-4	7	11	30.9	-31.9
-4	7	10	17.9	17.2
-4	7	9	26.2	25.1
-4	7	8	15.5	15.9
-4	7	7	49.5	-48.7
-4	7	5	53.5	-53.7
-4	7	4	22.6	25.0
-4	7	3	25.0	24.8
-4	7	2	18.4	-22.2
-4	6	21	21.7	-24.0
-4	6	20	16.0	-15.2
-4	6	17	18.6	21.3
-4	6	16	18.8	17.8
-4	6	15	41.9	-43.7
-4	6	14	29.9	-29.4
-4	6	13	28.5	27.6
-4	6	10	26.8	26.1
-4	6	9	44.1	-42.4
H	K	L	F OBS	F CALC
-4	6	9	37.5	-39.1
-4	6

H	K	L	F OBS	F CALC
-5	8	5	12.1	13.9
-5	8	4	34.2	32.7
-5	8	3	21.0	-19.8
-5	8	2	49.4	-37.0
-5	8	1	19.1	14.6
-5	7	15	17.2	-19.4
-5	7	14	47.5	24.5
-5	7	13	19.1	17.4
-5	7	12	19.7	-12.7
-5	7	11	43.1	-23.5
-5	7	9	30.2	2.7
-5	7	8	91.9	95.2
-5	7	7	41.5	-44.5
-5	7	6	42.0	-23.2
-5	7	5	90.3	-84.2
-5	7	4	11.7	12.1
-5	7	1	35.2	32.5
-5	6	19	43.6	-23.6
-5	6	18	18.1	-17.9
-5	6	17	41.6	21.7
-5	6	16	49.7	24.4
-5	6	15	42.0	-23.2
-5	6	14	11.0	-9.3
-5	6	13	13.7	10.1
-5	6	12	30.7	-32.5
-5	6	11	12.7	-12.3
-5	6	10	25.4	24.3
-5	5	22	47.3	-26.3
-5	5	20	40.7	31.4
-5	5	18	13.1	-15.4
-5	5	16	44.5	-25.1
-5	5	14	98.7	94.5
-5	5	12	49.8	-44.4
-5	5	9	97.0	-90.5
-5	5	8	94.9	91.7
-5	5	7	41.7	21.5
-5	5	6	98.3	-99.7
-5	4	24	42.4	32.3
-5	4	23	45.0	30.8
-5	4	22	24.6	23.2
-5	4	21	46.3	23.6
-5	4	19	49.2	-27.7
-5	4	18	19.5	13.6
-5	4	17	98.4	97.2
-5	4	16	11.4	-7.3
-5	4	15	19.3	-21.5
-5	4	14	98.7	94.5
-5	4	13	18.9	-21.1
-5	4	12	11.0	9.7
-5	4	11	71.1	70.7
-5	4	10	10.9	-12.9
-5	4	9	84.5	87.3
-5	4	8	12.7	12.7
-5	4	7	48.2	31.5
-5	4	6	11.0	-9.4
-5	4	5	46.6	47.4
-5	4	4	49.5	-23.0
-5	4	3	146.4	-144.4
-5	4	2	94.0	92.3
-5	4	1	75.5	71.2
-5	3	23	16.9	-16.5
-5	3	22	43.7	-27.0
-5	3	21	16.8	22.7
-5	3	20	38.0	46.7
-5	3	19	32.2	-33.8
-5	3	18	18.5	-19.2
-5	3	16	14.9	-17.5
-5	3	15	42.0	35.3
-5	3	14	47.2	42.1
-5	3	13	41.6	-38.7
-5	3	12	40.7	-42.4
-5	3	11	96.5	92.4
-5	3	9	72.8	70.5
-5	3	7	77.2	-73.7
-5	3	6	84.0	-87.7
-5	3	5	91.1	87.2
-5	3	4	99.4	93.7
-5	3	3	60.5	-51.5
-5	3	2	82.4	-85.6
-5	3	1	48.0	-57.2
-5	2	24	45.5	45.7
-5	2	23	11.0	10.7
-5	2	21	14.5	-16.8
-5	2	20	10.1	-11.4
-5	2	19	43.3	-25.0
-5	2	15	77.4	67.5
-5	2	17	49.1	31.1
-5	2	16	44.4	-44.5
-5	2	15	42.2	-23.4
-5	2	14	40.9	17.8
-5	2	12	23.1	30.9
-5	2	11	94.2	91.5
-5	2	10	74.5	-73.6
-5	2	9	43.4	-43.1
-5	2	8	91.9	94.0
-5	2	7	19.2	17.6
-5	2	5	25.5	32.2
-5	2	4	99.5	-99.6
-5	2	3	79.9	-79.0
-5	2	2	91.0	88.2
-5	2	1	98.1	94.7
-5	1	25	19.1	-18.7
-5	1	23	25.5	-24.2
-5	1	21	29.5	31.2
-5	1	20	41.3	-38.8
-5	1	19	42.6	-38.2
-5	1	18	11.0	-10.7
-5	1	17	15.0	-15.6
-5	1	16	13.7	-19.0
-5	1	15	19.7	17.3
-5	1	14	49.3	-39.9
-5	1	13	41.8	-36.6
-5	1	12	41.6	39.3
-5	1	11	97.6	-96.4
-5	1	10	12.9	-12.6
-5	1	9	84.9	-87.3
-5	1	8	12.7	-12.7
-5	1	7	130.9	-132.1
-5	1	6	59.1	-58.7
-5	1	5	91.4	89.4
-5	1	4	40.2	47.6
-5	1	3	44.7	36.2
-5	1	2	8.8	10.2

H	K	L	F OBS	F CALC
-4	1	1	102.6	-111.6
-4	0	24	29.0	-30.7
-4	0	24	39.8	39.2
-4	0	22	22.6	-19.6
-4	0	20	31.1	-32.9
-4	0	18	64.0	60.3
-4	0	16	59.7	-64.5
-4	0	12	73.8	69.4
-4	0	10	129.6	-139.3
-4	0	8	80.0	71.6
-4	0	6	69.8	65.1
-4	0	4	138.9	-144.1
-4	0	2	154.5	140.5
-4	9	3	19.8	-18.7
-4	9	1	39.1	40.1
-4	8	12	26.9	-24.2
-4	8	8	29.2	-29.0
-4	8	6	29.2	29.2
-4	8	4	29.1	29.2
-4	8	3	21.2	-17.9
-4	8	2	14.0	-13.9
-4	7	16	23.6	-21.7
-4	7	15	24.2	-22.2
-4	7	14	19.2	19.4
-4	7	11	11.6	9.7
-4	7	10	31.3	-32.5
-4	7	9	35.7	-37.1
-4	7	8	41.5	42.0
-4	7	7	15.4	-13.9
-4	7	6	13.3	-15.5
-4	7	5	15.1	-15.9
-4	7	4	15.9	-19.5
-4	7	3	20.4	24.2
-4	7	1	37.7	35.2
-4	6	19	26.3	-27.3
-4	6	17	22.8	21.8
-4	6	16	12.4	12.3
-4	6	13	35.7	-36.1
-4	6	12	11.9	-12.4
-4	6	11	47.7	44.3
-4	6	9	29.6	-26.2
-4	6	7	30.3	-32.3
-4	6	6	12.5	-11.5
-4	6	5	98.9	90.4
-4	6	4	11.1	9.9
-4	6	3	29.4	-31.0
-4	6	2	9.9	-14.6
-4	6	1	8.7	12.7
-4	5	20	10.9	9.0
-4	5	19	11.2	-10.9
-4	5	18	22.0	22.0
-4	5	17	13.1	12.6
-4	5	16	50.0	-50.2
-4	5	14	35.0	34.6
-4	5	13	17.7	19.6
-4	5	12	52.6	-45.8
-4	5	10	56.5	54.9
-4	5	9	11.3	-10.6
-4	5	8	56.5	54.9
-4	5	7	36.3	31.3
-4	5	6	26.2	-23.2
-4	5	5	25.7	20.1
-4	5	4	47.4	-23.3
-4	5	3	33.1	32.5
-4	5	2	55.2	54.9
-4	5	1	23.9	25.2
-4	4	21	29.1	31.2
-4	4	23	9.9	-4.8
-4	4	19	38.1	-35.0
-4	4	18	18.4	11.7
-4	4	17	30.1	32.6
-4	4	16	11.3	5.9
-4	4	15	28.8	28.0
-4	4	13	96.9	-72.9
-4	4	11	71.3	76.4
-4	4	10	12.6	10.2
-4	4	9	25.9	-24.9
-4	4	8	9.3	-12.6
-4	4	7	53.2	-49.4
-4	4	5	99.3	104.2
-4	4	4	27.3	-24.1
-4	4	3	62.8	-62.9
-4	4	2	47.4	47.8
-4	4	1	27.4	-30.5
-4	3	22	27.4	-30.5
-4	3	21	10.6	8.7
-4	3	20	15.5	14.2
-4	3	19	25.9	27.2
-4	3	17	28.1	-30.9
-4	3	16	54.4	-52.4
-4	3	15	23.6	24.0
-4	3	14	39.2	39.7
-4	3	13	9.8	-6.8
-4	3	12	27.4	-30.5
-4	3	11	39.2	39.7
-4	3	10	73.8	-71.8
-4	3	9	35.7	-37.1
-4	3	8	45.2	46.4
-4	3	7	29.1	29.2
-4	3	6	61.8	-61.6
-4	3	5	21.2	-17.9
-4	3	4	44.9	44.1
-4	3	3	39.1	40.1
-4	3	2	26.9	-24.2
-4	3	1	40.4	-37.7
-4	2	24	14.3	-13.9
-4	2	23	23.6	-21.7
-4	2	22	19.2	19.4
-4	2	21	29.2	-29.0
-4	2	20	13.4	-11.5
-4	2	19	45.4	45.1
-4	2	18	15.2	-15.9
-4	2	17	10.4	-9.3
-4	2	16	46.2	43.6
-4	2	15	15.1	-15.9
-4	2	14	13.3	-15.5
-4	2	13	46.2	-46.9
-4	2	12	47.5	47.9
-4	2	11	35.6	35.5
-4	2	10	45.2	-42.2
-4	2	9	27.8	-29.1
-4	2	7	33.2	-32.1
-4	2	6	77.6	71.6
-4	2	5	19.3	27.0
-4	2	4	99.5	-86.2
-4	2	3	38.6	41.5
-4	2	2	19.3	27.0
-4	2	1	18.5	21.7
-4	1	25	16.9	17.4
-4	1	24	14.5	13.3

H	K	L	F OBS	F CALC
-4	1	23	39.4	-39.0
-4	1	21	11.6	13.3
-4	1	20	11.5	15.1
-4	1	19	16.5	16.8
-4	1	18	8.8	-3.8
-4	1	17	55.6	-52.6
-4	1	16	19.1	-20.9
-4	1	15	65.4	62.3
-4	1	14	44.9	-42.6
-4	1	13	20.9	24.0
-4	1	12	20.7	-20.8
-4	1	11	32.2	-31.5
-4	1	10	42.4	-41.2
-4	1	9	106.0	104.3
-4	1	8	36.0	26.3
-4	1	7	74.1	-68.5
-4	1	6	47.9	-47.6
-4	1	5	22.0	24.1
-4	1	4	29.2	-29.0
-4	1	3	73.8	-71.8
-4	1	2	113.2	-111.8
-4	1	1	45.2	44.2
-4	0	24	19.2	19.5
-4	0	20	36.7	-38.4
-4	0	18	40.6	38.2
-4	0	16	12.5	-10.4
-4	0	14	45.2	-40.1
-4	0	12	44.2	50.5
-4	0	10	73.8	-71.8
-4	0	8	62.9	74.4
-4	0	6	113.2	-111.8
-4	0	4	41.5	37.1
-4	0	2	34.5	29.8
-4	8	7	18.0	-14.4
-4	7	13	38.5	-37.3
-4	7	8	12.2	11.0
-4	7	4	24.3	22.4
-4	6	8	14.4	14.9
-4	6	1	13.2	-13.6
-4	5	15	42.3	23.9
-4	5	13	40.5	12.7
-4	5	11	17.4	-14.4
-4	5	9	49.3	46.5
-4	5	7	9.8	7.9
-4	5	5	37.7	-49.7
-4	5	3	47.3	26.4
-4	4	6	47.3	-26.2
-4	4	2	11.7	-12.9
-4	4	1	26.1	-27.4
-4	3	16	18.7	20.4
-4	3	15	18.8	-17.2
-4	3	14	41.6	-39.9
-4	3	13	16.8	19.0
-4	3	12	28.2	27.9
-4	3	10	18.4	17.2
-4	3	9	21.6	-23.2
-4	3	8	98.3	-95.7
-4	3	7	20.5	22.5
-4	3	6	44.6	44.4
-4	3	5	45.4	-42.3
-4	3	4	21.4	-23.7
-4	3	3	13.7	11.7
-4	3	2	45.6	-45.9
-4	3	1	29.2	29.2
-4	2	20	14.8	15.7
-4	2	19	21.7	21.5
-4	2	18	29.7	-26.2
-4	2	17	28.3	-29.8
-4	2	16	21.2	17.5
-4	2	12	19.6	-19.7
-4	2	11	12.5	-14.4
-4	2	10	29.3	33.4
-4	2	9	9.4	11.6
-4	2	8	23.5	-24.5
-4	2	6	25.2	-29.8
-4	2	5	19.9	-22.3
-4	2	4	50.7	52.9
-4	2	3	37.5	38.9
-4	2	2	33.3	-27.9
-4	2	1	28.7	25.1
-4	1	20	15.8	-13.0
-4	1	17	14.5	15.7
-4	1	15	41.2	-41.5
-4	1	13	36.4	36.4
-4	1	12	8.6	10.4
-4	1	9	30.6	-29.3
-4	1	8	13.7	-16.1
-4	1	7	40.4	44.1
-4	1	6	33.2	35.3
-4	1	5	47.9	-49.1
-4	1	4	27.2	-29.3
-4	1	3	9.4	-12.0
-4	1	2	18.3	-15.4
-4	1	1	33.5	37.6
-4	0	20	19.3	19.2
-4	0	18	24.0	-29.4
-4	0	16	34.9	35.4
-4	0	12	24.5	-27.4
-4	0	10	40.6	41.8
-4	0	8	34.9	-33.4
-4	0	6	24.4	-19.4
-4	0	4	59.3	61.2
-4	0	2	93.6	-89.4
-4	9	3	39.1	33.2
-4	9	1	22.7	25.0
-4	8	8	21.4	21.3
-4	8	5	32.9	-34.5
-4	8	4	19.4	-18.4
-4	8	2	14.8	-11.8
-4	7	12	12.1	8.1
-4	7	10	32.1	32.5
-4	7	8	35.6	-37.4
-4	7	6	11.2	9.2
-4	7	4	9.2	-9.5
-4	7	1	33.5	37.6
-4	6	20	19.3	19.2
-4	6	18	24.0	-29.4
-4	6	16	34.9	35.4
-4	6	12	24.5	-27.4
-4	6	10	40.6	41.8
-4	6	8	34.9	-33.4
-4	6	6	24.4	-19.4
-4	6	4	59.3	61.2
-4	6	2	93.6	-89.4
-4	5	13	39.1	33.2
-4	5	11	22.7	25.0
-4	5	8	21.4	21.3
-4	5	6	32.9	-34.5
-4	5	4	19.4	-18.4
-4	5	2	14.8	-11.8
-4	5	1	12.1	8.1
-4	4	12	32.1	32.5
-4	4	10	35.6	-37.4
-4	4	8	11.2	9.2
-4	4	6	9.2	-9.5
-4	4	1	33.5	37.6
-4	3	20	19.3	19.2
-4	3	18	24.0	-29.4
-4	3	16	34.9	35.4
-4	3	12	24.5	-27.4
-4	3	10	40.6	41.8
-4	3	8	34.9	-33.4
-4	3	6	24.4	-19.4
-4	3	4	59.3	61.2
-4	3	2	93.6	-89.4
-4	2	13	39.1	33.2
-4	2	11	22.7	25.0
-4	2	8	21.4	21.3
-4	2	5	32.9	-34.5
-4	2	4	19.4	-18.4
-4	2	2	14.8	-11.8
-4	2	1	12.1	8.1
-4	1	12	32.1	32.5
-4	1	10	35.6	-37.4
-4	1	8	11.2	9.2
-4	1	6	9.2	-9.5

TABLE 34

$Cd(quin)_2(NO_3)_2(H_2O)$

Atom positions (fractional coordinates)

	x/a	y/b	z/c
Cd	0.13619(5)	0.05436(6)	0.31853(2)
C(1)	-0.0118(7)	-0.2073(8)	0.3771(3)
C(2)	-0.0704(8)	-0.3047(9)	0.4157(4)
C(3)	-0.0326(8)	-0.2985(9)	0.4696(4)
C(4)	0.0666(8)	-0.1955(10)	0.4871(3)
C(5)	0.1098(9)	-0.1855(10)	0.5430(4)
C(6)	0.2030(10)	-0.0876(12)	0.5550(5)
C(7)	0.2574(9)	-0.0007(11)	0.5142(4)
C(8)	0.2173(8)	-0.0069(10)	0.4596(4)
C(9)	0.1197(7)	-0.1042(9)	0.4447(3)
C(10)	0.3969(8)	0.1969(9)	0.3055(4)
C(11)	0.5251(8)	0.2216(11)	0.2993(4)
C(12)	0.6004(8)	0.0939(12)	0.3096(4)
C(13)	0.5522(8)	-0.0476(9)	0.3260(4)
C(14)	0.6250(8)	-0.1808(12)	0.3369(5)
C(15)	0.5746(10)	-0.3159(11)	0.3528(5)
C(16)	0.4489(9)	-0.3312(10)	0.3583(5)
C(17)	0.3725(8)	-0.2053(9)	0.3474(4)
C(18)	0.4238(8)	-0.0594(9)	0.3311(4)
O(1)	0.1683(6)	0.0736(7)	0.2152(3)
O(2)	0.1517(5)	-0.1564(7)	0.2508(2)
O(3)	0.1825(7)	-0.1299(9)	0.1612(3)
O(4)	0.1203(7)	0.3261(7)	0.2972(3)
O(5)	0.1453(7)	0.2869(9)	0.3859(3)
O(6)	0.1521(8)	0.5226(9)	0.3526(4)
O(7)	-0.0663(6)	0.0536(7)	0.2862(3)
N(1)	0.0769(6)	-0.1093(8)	0.3893(3)
N(2)	0.3475(7)	0.0648(8)	0.3198(3)
N(3)	0.1674(6)	-0.0685(7)	0.2075(3)
N(4)	0.1394(7)	0.3837(9)	0.3465(3)

TABLE 35

$Cd(quin)_2(NO_3)_2(H_2O)$

(a) Anisotropic temperature factors ($Å^2$) *

	U_{11}	U_{22}	U_{33}	$2U_{32}$	$2U_{31}$	$2U_{12}$
Cd	0.037	0.037	0.037	0.002	-0.002	-0.003
C(1)	0.050	0.026	0.043	0.011	-0.010	0.004
C(2)	0.047	0.041	0.064	0.002	0.009	-0.012
C(3)	0.051	0.056	0.048	0.030	0.035	0.001
C(4)	0.053	0.057	0.033	0.023	0.016	0.035
C(5)	0.071	0.062	0.044	0.001	-0.013	0.020
C(6)	0.070	0.098	0.044	-0.013	-0.024	0.045
C(7)	0.057	0.077	0.045	-0.008	-0.037	0.012
C(8)	0.045	0.051	0.053	-0.006	-0.016	-0.002
C(9)	0.042	0.043	0.038	-0.002	-0.002	0.020
C(10)	0.048	0.059	0.047	0.007	-0.016	0.004
C(11)	0.048	0.062	0.065	0.001	0.013	-0.035
C(12)	0.033	0.078	0.058	-0.002	-0.001	-0.017
C(13)	0.042	0.069	0.037	-0.024	0.011	-0.001
C(14)	0.044	0.082	0.063	-0.042	-0.012	0.023
C(15)	0.067	0.056	0.069	-0.003	-0.006	0.045
C(16)	0.059	0.058	0.068	0.017	0.011	0.037
C(17)	0.047	0.040	0.053	0.019	0.004	0.013
C(18)	0.041	0.056	0.039	0.004	0.008	0.003
O(1)	0.053	0.054	0.052	0.002	-0.004	-0.003
O(2)	0.050	0.038	0.048	0.009	-0.008	-0.015
O(3)	0.095	0.063	0.045	-0.022	0.007	0.002
O(4)	0.066	0.043	0.066	-0.016	-0.030	0.003
O(5)	0.070	0.069	0.063	0.009	0.019	0.023
O(6)	0.094	0.038	0.099	-0.041	-0.023	0.019
O(7)	0.043	0.040	0.071	0.001	-0.005	0.008
N(1)	0.038	0.034	0.032	0.001	0.004	-0.005
N(2)	0.044	0.048	0.039	0.014	0.004	-0.014
N(3)	0.038	0.041	0.032	-0.005	-0.010	-0.002
N(4)	0.048	0.034	0.067	-0.007	0.013	0.004

TABLE 35 (cont)

(b) Mean estimated standard deviations ($Å^2$)

	$\underline{U}_{11}$	$\underline{U}_{22}$	$\underline{U}_{33}$	$2\underline{U}_{32}$	$2\underline{U}_{31}$	$2\underline{U}_{12}$
Cd	0.0003	0.0003	0.0003	0.0004	0.0005	0.0004
C	0.004	0.004	0.005	0.008	0.008	0.008
O	0.004	0.003	0.003	0.006	0.007	0.006
N	0.003	0.003	0.003	0.006	0.006	0.005

* These are the values of U_{ij} in equation (5) (Section I.1.4(b)).

TABLE 36

$Cd(quin)_2(NO_3)_2(H_2O)$

Hydrogen positions * (fractional coordinates) and isotropic temperature factors ($Å^2$)

H(1) C(1)	-0.030(12)	-0.209(15)	0.346(5)	0.06(5)
H(2) C(2)	-0.138(12)	-0.396(17)	0.407(6)	0.07(3)
H(3) C(3)	-0.062(12)	-0.354(16)	0.491(6)	0.06(3)
H(5) C(5)	0.081(12)	-0.286(17)	0.558(6)	0.07(3)
H(6) C(6)	0.225(14)	-0.084(15)	0.597(6)	0.07(4)
H(7) C(7)	0.323(14)	0.066(15)	0.519(6)	0.03(4)
H(8) C(8)	0.241(13)	0.064(14)	0.443(6)	0.05(4)
H(10) C(10)	0.345(12)	0.281(16)	0.294(5)	0.05(3)
H(11) C(11)	0.549(12)	0.310(15)	0.289(5)	0.03(4)
H(12) C(12)	0.694(14)	0.077(17)	0.304(6)	0.05(4)
H(14) C(14)	0.723(12)	-0.171(17)	0.330(6)	0.06(4)
H(15) C(15)	0.635(13)	-0.392(16)	0.357(6)	0.06(4)
H(16) C(16)	0.429(13)	-0.443(14)	0.370(6)	0.07(4)
H(17) C(17)	0.290(12)	-0.235(16)	0.361(6)	0.07(4)
H(19) O(7)	-0.065(8)	-0.011(10)	0.256(4)	0.04(2)
H(20) O(7)	-0.087(9)	0.133(9)	0.274(4)	0.10(2)

* Hydrogens are bonded to atoms shown in square brackets

APPENDIX VIII

COMPARISONS OF THE PLANARITY AND ASYMMETRY OF THE NITRATE GROUPS IN THE COMPLEXES STUDIED

a) Nitrate Planes

If we consider the metal atom to have directional orbitals then these may be defined as lying in the plane containing the metal atom and two closest oxygen atoms (M, O(1), O(2)). Therefore, it is of interest to measure the dihedral angle between this plane and the plane of the nitrate group. These angles are listed in Table 37, and the results are also presented graphically in Figure 1 where the angles are plotted against the deviation of the metal atom from the nitrate plane. The large spread of values suggests that some correlation exists with the distortions in the nitrate groups caused by steric interaction from neighbouring moieties. Thus, in the complex $[Cu(py)_2(NO_3)_2]_2py$, the nitrate group involved in dimerisation shows a large dihedral angle (8.12^{o}) while the remaining nitrate has no such external bonding and only exhibits a small distortion. Similarly, the hydrogen bonding in $Ni(py)_2(NO_3)_2(H_2O)_2$ and the steric overcrowding in the tris-pyridine complexes also result in relatively large distortions. However, an exception to this trend is the complex $Cd(quin)_2(NO_3)_2(H_2O)$ in which both nitrate groups

might be expected to display similar distortions. The latter result is not unexpected since, in this complex, the nitrate groups do not follow the expected trend in N-O distances and it is suggested that this may be caused by the hydrogen bonding or other intermolecular interaction (Section III.2.2).

Another feature of interest in the nitrate planes is the positioning of the atoms in relationship to these planes. In all of the complexes studied, the nitrogen atom is always on the opposite side of the nitrate plane to the oxygen atoms and, in most cases, it occupies the same side as the metal atom. When the metal and nitrogen atoms are not similarly positioned, the planes of the nitrate groups only show small distortions from the metal orbitals planes. The one exception to this is again the complex $Cd(quin)_2(NO_3)_2(H_2O)$ in which one of the nitrate groups shows a large distortion while the metal and nitrogen atoms lie on opposite sides of the nitrate plane.

b) Nitrate Asymmetry

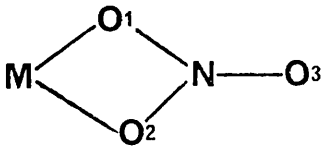
The relevant parameters to describe the asymmetry of the nitrate groups in the complexes examined are tabulated in Table 38 and the results are presented graphically in Figure 2.

In the tris-pyridine complexes, the asymmetry increases from Cd to Cu. However, the asymmetry of $Cu(py)_3(NO_3)_2$ is greater than the series would predict and this has

been explained using the Jahn-Teller theorem (Section II. 2.2). The difference in M-O distances found in the latter complex (0.58 Å) is of the same order as that found in the other copper complexes studied. The exceptions to this are one of the nitrate groups in Form I of $Cu(\alpha\text{-pic})_2(NO_3)_2$ where the asymmetry is smaller and the greater asymmetry in the nitrate group involved in dimerisation in $[Cu(py)_2(NO_3)_2]_2py$. However, in the absence of external factors, asymmetry in the nitrate groups of 0.5 - 0.6 Å would appear to be a favourable situation in copper(II) nitrate complexes.

TABLE 37

PLANARITY OF THE NITRATE GROUPS



Distance of atoms from planes (Å)

a = M, b = O(1), c = O(2), d = O(3), e = N(1)

Dihedral angle between planes [M, O(1), O(2)] and [O(1), O(2), O(3), N(1)] = f°

COMPLEX	a	b	c	d	e	f	
1(a)	0.136	0.008	0.009	0.009	-0.026	0.165	*
1(b)	-0.287	0.001	0.001	0.001	-0.001	8.115	
2(a)	-0.164	0.001	0.001	0.001	-0.003	4.981	
2(b)	0.059	-0.001	-0.001	-0.001	0.004	1.743	*
3(a)	-0.081	-0.002	-0.003	-0.003	0.007	2.295	*
3(b)	-0.097	-0.005	-0.005	-0.006	0.162	2.722	*
4(a)	-0.291	0.005	0.005	0.005	-0.015	8.440	
4(b)	-0.129	-0.001	-0.001	-0.001	0.003	3.616	*
5	-0.216	0.001	0.001	0.001	-0.004	5.997	
6	0.263	-0.005	-0.005	-0.005	0.014	7.257	
7	0.318	-0.002	-0.002	-0.002	0.007	8.900	
8	0.267	-0.002	-0.002	-0.002	0.006	7.748	
9	-0.292	0.004	0.004	0.005	-0.013	7.653	
10(a)	-0.020	-0.005	-0.005	-0.005	0.014	0.906	*
10(b)	0.338	0.003	0.003	0.004	-0.010	8.266	*

* Metal and nitrogen atoms on the same side of the nitrate plane.

1 $[Cu(py)_2(NO_3)_2]_2py$

2 $Cu(\alpha\text{-pic})_2(NO_3)_2$ Form I

3 $Cu(\alpha\text{-pic})_2(NO_3)_2$ Form II

4 $Zn(py)_2(NO_3)_2$

5 $Ni(py)_2(NO_3)_2(H_2O)_2$

6 $Cu(py)_3(NO_3)_2$

7 $Zn(py)_3(NO_3)_2$

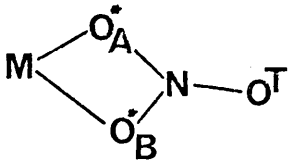
8 $Co(py)_3(NO_3)_2$

9 $Cd(py)_3(NO_3)_2$

10 $Cd(quin)_2(NO_3)_2(H_2O)$

TABLE 38

ASYMMETRY OF THE NITRATE GROUPS



M-O* = a, (N-O*) - (N-O^T) = b, O*-N-O^T = c, ($M-O^*_A$) - ($M-O^*_B$) = d, M-O*-N = e, ($M-O^*_A$-N) - ($M-O^*_B$-N) = f

COMPLEX	a	b	c	d	e	f
1(a)	2.035(6)	0.111	124.5(9)	0.573	105.8(5)	25.1
	2.618(8)	0.045	117.1(8)		80.7(5)	
1(b)	2.042(6)	0.137	124.7(8)	0.864	114.0(5)	37.5
	2.906(7)	0.001	116.3(8)		76.5(5)	
2(a)	2.026(16)	0.03	129.6(16)	0.281	100.1(11)	12.6
	2.507(13)	0.03	116.3(16)		87.5(10)	
2(b)	1.971(13)	0.07	129.3(15)	0.518	111.7(10)	24.1
	2.489(14)	0.00	124.7(15)		87.6(10)	
3(a)	1.983(10)	0.08	125.3(12)	0.534	107.2(8)	24.2
	2.517(8)	0.04	120.1(12)		83.0(8)	
3(b)	2.005(10)	0.08	125.9(13)	0.546	106.5(9)	24.6
	2.551(7)	0.03	117.4(13)		81.9(8)	
4(a)	2.044(12)	0.002	120.5(13)	0.714	110.6(9)	33.6
	2.758(19)	0.005	120.1(17)		77.0(11)	
4(b)	2.048(13)	0.066	123.5(14)	0.706	112.4(10)	32.3
	2.754(14)	0.005	120.4(14)		80.1(9)	
5	2.101(2)	0.009	117.4(3)	1.143	127.0(2)	57.6
	3.244(3)	-0.036	121.0(3)		69.4(2)	
6	2.154(7)	0.029	123.0(9)	0.578	109.9(6)	27.6
	2.732(5)	0.016	119.7(9)		82.3(6)	
7	2.232(13)	0.05	126.0(12)	0.186	101.0(9)	8.4
	2.418(12)	0.03	121.4(14)		92.6(8)	
8	2.207(9)	0.064	125.0(11)	0.104	98.0(7)	6.4
	2.311(9)	0.012	121.0(10)		91.6(6)	
9	2.444(9)	0.050	121.9(12)	0.047	97.4(6)	2.3
	2.491(10)	0.048	122.6(11)		95.1(7)	
10(a)	2.431(8)	0.049	119.0(8)	0.064	95.9(6)	1.7
	2.495(7)	0.001	123.2(8)		94.2(5)	
10(b)	2.391(7)	0.075	120.6(7)	0.170	100.0(5)	7.2
	2.561(8)	0.042	124.0(8)		92.8(6)	

FIGURE 1

DEVIATIONS OF THE NITROGEN PLANES FROM THE METAL

ORBITALS PLANES

A key to the numbering of the complexes is given in Table 37

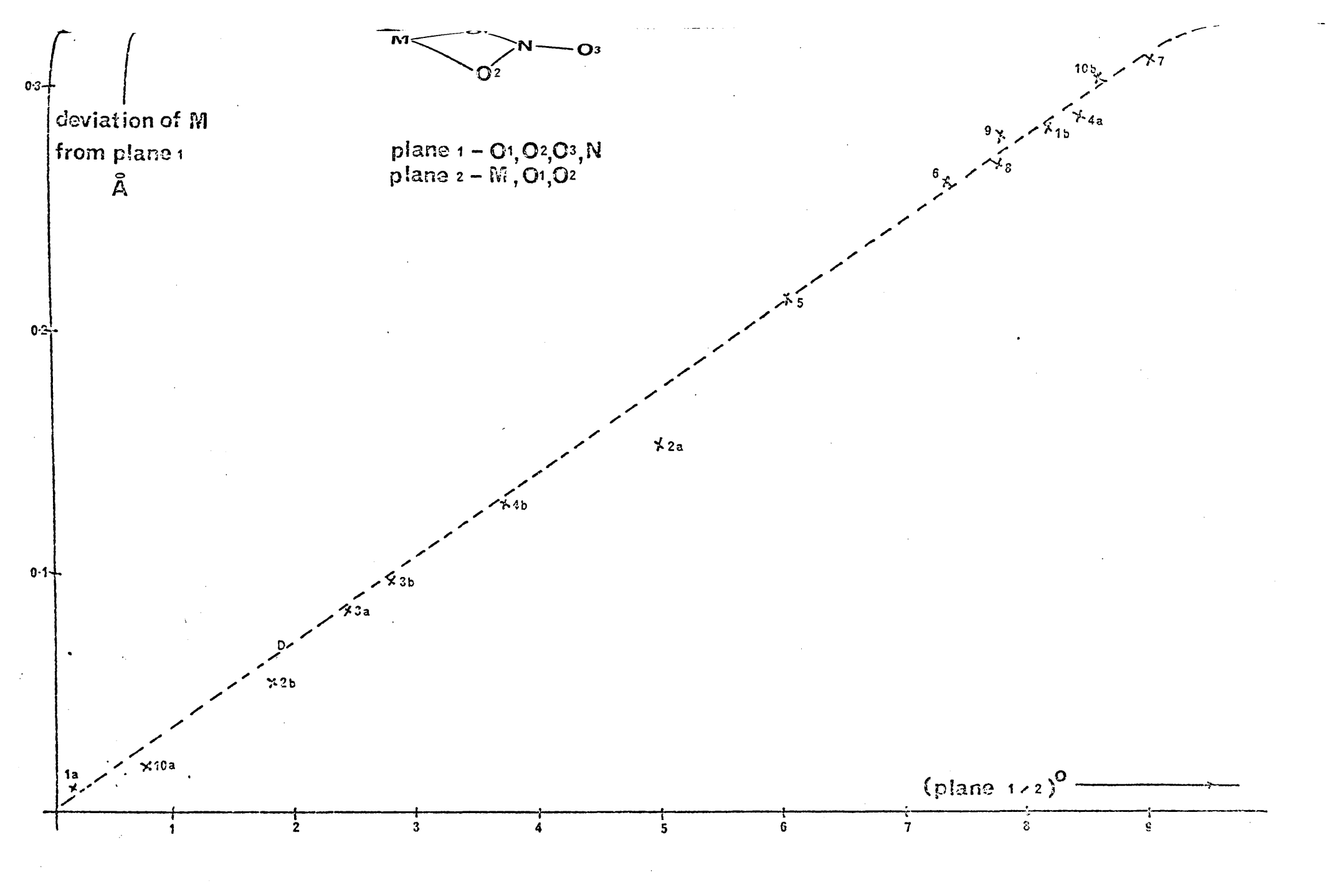
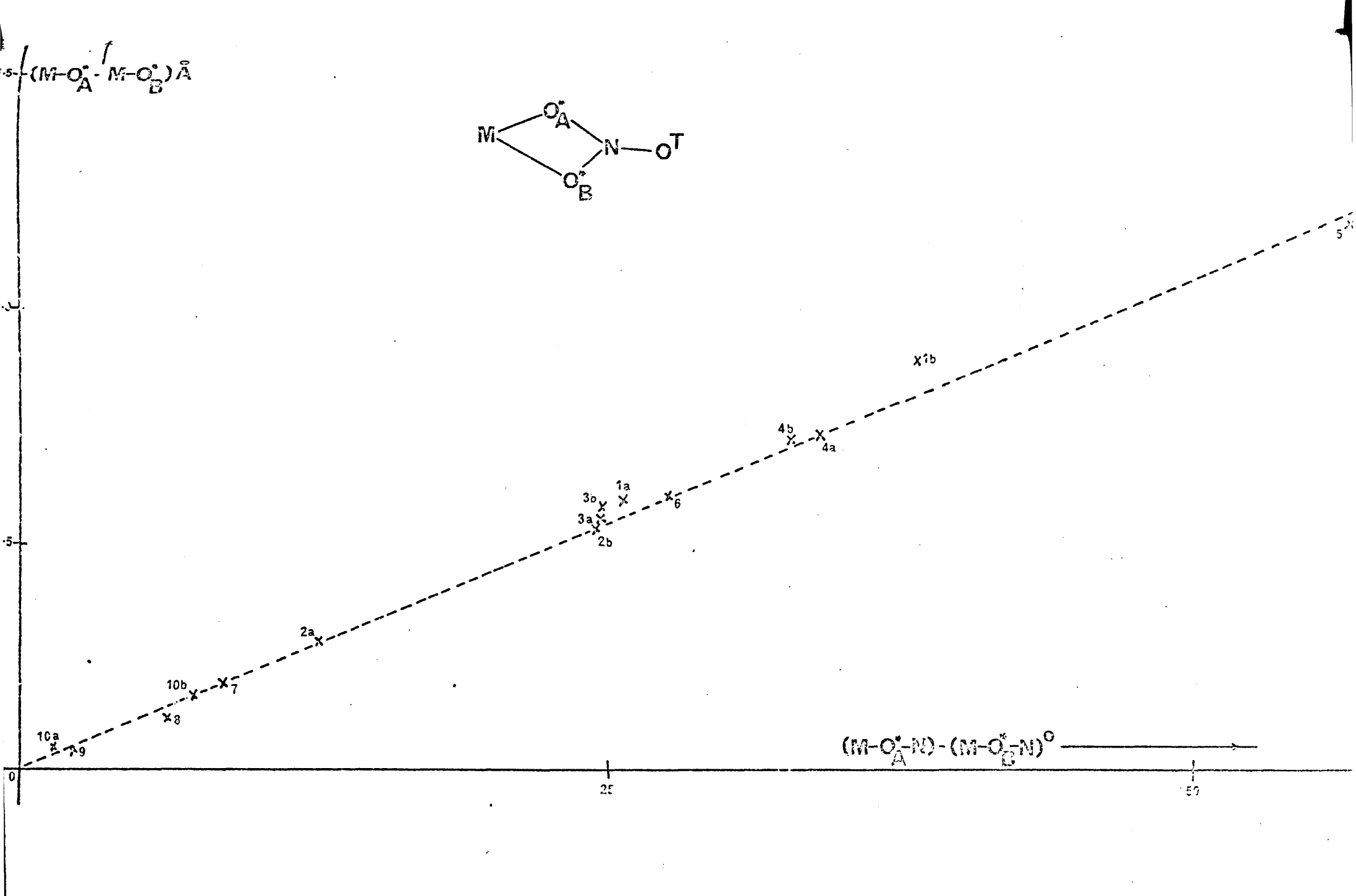

M
N
O3
O2
deviation of M
from plane 1
Å
plane 1 – O1,O2,O3,N
plane 2 – M , O1,O2
0·3
0·2
0·1
1a
10a
2b
D
3a
3b
4b
2a
5
6
8
9
1b
4a
10b
7
(plane 1 ^ 2)°
1
2
3
4
5
6
7
8
9

FIGURE 2

THE ASYMMETRY OF THE NITRATE GROUPS IN THE COMPLEXES STUDIED

A key to the numbering of the complexes is given in Table 37


(M-O°A - M-O°B) Å
M
O°A
N
OT
O°B
1a
1b
2a
2b
3a
3b
4a
4b
5
6
7
8
9
10a
10b
(M-O°A-N) - (M-O°B-N)°
0
25
50

REFERENCES

(1) J.M. Robertson, Helv.Chim.Acta, 1972 55 119
G.A. Jeffrey, D.W.J. Cruickshank, E.G. Cox, Quart.Rev., 1953 7 335
P.P. Ewald (ed), 'Fifty Years of X-Ray Diffraction,' International Union of Crystallography, 1962

(2) M. von Laue, Sitzber.Math.Physik.Kl.Bayer.Akad. Wiss., Muenchen, 1912 303
Reprinted in Naturwiss, 1952 361, 368

(3) W.L. Bragg, Proc.Cambridge Phil.Soc., 1913 17 43

(4) M.J. Buerger, 'Crystal-Structure Analysis', Wiley, New York, 1960

(5) G.H. Stout and L.H. Jensen, 'X-Ray Structure Determination', MacMillan, New York, 1968

(6) U.W. Arndt and B.T.M. Williams, 'Single-Crystal Diffractometry', C.U.P., Cambridge, 1966

(7) M.M. Woolfson, 'An Introduction to X-Ray Crystallography', C.U.P., Cambridge, 1970

(8) M.J. Buerger, 'The Precession Method', Wiley, New York, 1964

(9) J.M. Robertson, 'Organic Crystals and Molecules', Cornell University Press, New York, 1953

(10) 'International Tables for X-Ray Crystallography', Vol.III, C.H. Macgillavry and G.D. Rieck (eds.),

Kynoch Press, Birmingham, 1962

(11) J.M. Bijvoet, Proc.Acad.Sci.Amst., 1949 52 313
H. Lipson and W. Cochran, 'The Determination of Crystal Structure', G. Bell, 1966

(12) A. Herzenberg and H.S.M. Lau, Acta Cryst., 1967 22 24

(13) D.W.J. Cruickshank, 'The Equations of Structure Refinement', The University, Glasgow, 1964
D.W.J. Cruickshank, Acta Cryst., 1965 19 153

(14) G. Tunnel, Amer.Min., 1939 24 448

(15) A.L. Patterson, Phys.Rev., 1934 46 372
Z.Kristallogr., 1935 90 517

(16) G.A. Sim in 'Computing Methods and the Phase Problem in X-Ray Crystal Analysis', Ed., R. Pepinsky, J.M. Robertson and J.C. Speakman, Pergamon Press, Oxford, 1961, p227

(17) D. Harker and J.S. Kasper, Acta Cryst., 1948 1 70

(18) D. Sayre, Acta Cryst., 1952 5 60

(19) W. Cochran and M.M. Woolfson, Acta Cryst., 1955 8 1

(20) W.H. Zachariasen, Acta Cryst., 1952 5 68

(21) J. Karle and H. Hauptman, Acta Cryst., 1950 9 635
I.L. Karle and J. Karle, Acta Cryst., 1964 17 835
Acta Cryst., 1966 21 849

(22) J. Karle and H. Hauptman, Acta Cryst., 1956 9 635

(23) A.D. Booth, Proc.Roy.Soc., 1946 A188 77
Ibid., 1947 A190 482

(24) S.F. Darlow, Acta Cryst., 1960 13 683

(25) A. Guntz and F. Martin, Bull.Soc.Chim., France 1909 5 1004

(26) M. Schmeisser and D. Lutzow, Agnew Chem., 1954 66 230

(27) C.C. Addison and B.J. Hathaway, J. Chem.Soc., 1958 3099

(28) D.K. Straub, R.S. Drago and J.T. Donoghue, Inorg. Chem., 1962 1 848

(29) B.O. Field and C.J. Hardy, Quart.Rev., 1964 18 361

(30) C.C. Addison and N. Logan, Adv.Inorg.Chem.Radiochem., 1964 6 71

(31) C.C. Addison and D. Sutton, Prog.Inorg.Chem., 1967 8 195

(32) L.R. Maxwell and V.M. Mosley, J.Chem.Phys., 1940 8 738

(33) L. Pauling and L.O. Brockway, J. Amer.Chem.Soc., 1937 59 13

(34) J.C.D. Brand and T.M. Cawthon, J. Amer.Chem.Soc., 1955 77 319

(35) J.E. Fleming and H. Lynton, Chem.Ind(London)., 1960 1415

(36) C.C. Addison, N. Logan, S.C. Wallwork and C.D. Garner, Quart.Rev., 1972 26 289

(37) C.C. Addison, Coord.Chem.Rev., 1966 1 588

(38) J. Powell and B.L. Shaw, J.Chem.Soc., 1965 3879

(39) F.J. Hopton, A.J. Rest, D.T. Rosevear and F.G.A. Stone, reported in Reference (36)

(40) C.C. Addison and D. Sutton, J.Chem.Soc., 1966 1524

(41) M. Mathew, G.L. Palenik and A.J. Corty, Cand.J. Chem., 1971 49 4119

(42) S. Scavnicar and B. Matkovic, Acta Cryst., 1969 25 2046

(43) M.S. Hussain and H. Hope, Acta Cryst., 1969 25 1866

(44) J. Garaj, Acta Chem.Scand., 1968 22 1710
B. Morosin, Acta Cryst., 1970 B26 1203

(44a) B. Matkono, B. Ribar, B. Zelenco and S.W. Peterson, Acta Cryst., 1966 21 719

(45) B. Duffin, Acta Cryst., 1968 B24 396

(46) A. Santoro, A.D. Mighell and C.W. Reimann, Acta Cryst., 1970 B26 979

(47) G.G. Messmer and G.L. Palenik, Inorg.Chem., 1969 8 2750

(48) R.E. La Villa and S.H. Bauer, J.Amer.Chem.Soc., 1963 85 3597

(49) C.D. Garner and S.C. Wallwork, J.Chem.Soc., 1966 1496

(50) J. Hilton and S.C. Wallwork, Chem.Comm., 1968 871

(51) T.J. King, N. Logan, A. Morris and S.C. Wallwork, Chem.Comm., 1971 554

(52) J. Drummond and J.S. Wood, J.Chem.Soc(A)., 1970 226

(53) A. Zalkin, J.D. Forrester and D.H. Templeton, J.Chem.Phys., 1963 39 2881

(54) S. Scavnicar and B. Prodic, Acta Cryst., 1965 18 698

(55) C.D. Garner, D. Sutton and S.C. Wallwork, J.Chem.Soc(A)., 1967 1949

(56) A.R. Al-Karaghouli and J.S. Wood, Chem.Comm., 1970 135

(57) T.A. Beineke and J. Delgaudia, Inorg.Chem., 1968 7 715

(58) G.A. Barclay, T.M. Sabine and J.C. Taylor, Acta Cryst., 1965 19 205

(59) S.S. Makic and L.M. Marojlovic, Bull.Inst.Nuclear Sci.,'Boris Kidrich'(Belgrade), 1965 11 135

(60) T. Veki, A. Zalkin and D.H. Templeton, Acta Cryst., 1966 20 836

J.C. Taylor, M.H. Mueller and R.L. Hitterman, Acta Cryst., 1966 20 842

D. Britton and J.D. Dunitz, Acta Cryst., 1965 19 815

(61) G. Johansson, Acta Chem.Scand., 1968 22 389

(62) D. Hall, A.D. Rae and T.N. Waters, Acta Cryst., 1965 19 389
J.C. Taylor and M.H. Mueller, Acta Cryst., 1965 19 536

(63) G.F. Volodina, I.M. Rumanova and N.V. Belov, Soviet Phys.Cryst., 1961 6 741

(64) F.A. Cotton and R.H. Soderberg, J.Amer.Chem.Soc., 1963 85 2402

(65) L.F. Power and A.M. Tait, Inorg.Nucl.Chem.Letters, 1971 7 337

(66) A.R. Al-Karaghouli and J.S. Wood, J.Amer.Chem.Soc., 1968 90 6548

(67) D.S. Moss and S.P. Sinha, Z.phys.Chem.(Frankfurt), 1969 63 190

(68) C. Panattoni, R. Graziani, U. Croatto, B. Zarli, and G. Bombieri, Inorg.Chim.Acta, 1968 2 43

(69) Mazhar-ul-Haque, F.A. Hart and C.N. Caughlan, Chem.Comm., 1970 1240

(70) F.W.B. Einstein, E. Enwall, D.M. Morris and D. Sutton, Inorg.Chem., 1971 10 678

(71) A.F. Cameron, R.H. Nuttall and D.W. Taylor, J.Chem.Soc.(Dalton), 1972 in press

(72) G. Bonieri, E. Forsellini, R. Grazioni and E. Tendello, J.Chem.Soc(A)., 1970 3349

(73) J.G. Bergman and F.A. Cotton, Inorg.Chem., 1966 5 1208

(74) J. Hilton and S.C. Wallwork, reported in Reference (36)

(75) A.F. Cameron, K.P. Forrest, R.H. Nuttall and D.W. Taylor, Chem.Comm., 1970 210

(76) A.F. Cameron, K.P. Forrest, R.H. Nuttall and D.W. Taylor, J.Chem.Soc(A)., 1971 2492

(77) A.F. Cameron, R.H. Nuttall and D.W. Taylor, Chem. Comm., 1970 865

(78) A.F. Cameron, R.H. Nuttall and D.W. Taylor, Chem. Comm., 1971 253

(79) A.F. Cameron, R.H. Nuttall and D.W. Taylor, J.Chem. Soc.(Dalton), 1972 58

(80) A.F. Cameron, R.H. Nuttall and D.W. Taylor, Chem. Comm., 1971 129

(81) A.F. Cameron, R.H. Nuttall and D.W. Taylor, J.Chem. Soc.,(Dalton), 1972 in press

(82) A.F. Cameron, R.H. Nuttall and D.W. Taylor, J.Chem. Soc.(Dalton), 1972 in preparation

(83) A.N. Khodchenkov, V. Spiridonov and P.H. Asishin, Zhur.Strukt.Khim., 1965 6 765

(84) G.W. Bushnell and M.A. Khan, Cand.J.Chem., 1972 50 315

(85) B. Kamenar, Acta Cryst., 1969 B25 800

(86) C.D. Garner and S.C. Wallwork, Chem.Comm., 1969 108; J.Chem.Soc(A)., 1970 3092

(87) P. Gallezot, D. Weigel and M. Prettre, Acta Cryst., 1967 22 699

(88) B. Ribar, M. Sljukic, B. Matkovic, F. Gabela and E. Girt, Acta Cryst., 1967 23 1113

(89) J. Hilton and S.C. Wallwork, reported in Reference (36)

(90) D.A. Langs, C.R. Hare and R.G. Little, Chem.Comm., 1967 1080

(91) F.W.B. Einstein, E. Enwall, D.M. Morris and D. Sutton, Inorg.Chem., 1971 10 678

(92) N.A. Bailey and S.J. Bowler, J.Chem.Soc(A)., 1971 1763

(93) H. Nakai, S. Ooi and H. Kuroya, Bull.Chem.Soc. (Japan), 1970 43 577

(94) R.E. Drew and F.W.B. Einstein, Acta Cryst., 1972 B28 345

(95) A.F. Cameron, R.H. Nuttall and D.W. Taylor, J.Chem. Soc.(Dalton), 1972 422

(96) A.F. Cameron, R.H. Nuttall and D.W. Taylor, J.Chem. Soc(A)., 1971 3402

(97) E.B. Fleischer and E. Klem, Inorg.Chem., 1965 4 637

(98) S.C. Wallwork and W.E. Addison, J.Chem.Soc., 1965 2925

(99) L. Berger and J.A. Friedberg, Phys.Rev., 1964 136A 158

(100) B. Ribar, W. Nowacki, M. Sljukic, S. Scavnicar and F. Gabela, Z. Kristallogr., 1969 129 304

(101) W. Nowacki and R. Schiedeggar, Helv.Chim.Acta., 1952 35 375

(102) B. Duffin and S.C. Wallwork, Acta Cryst., 1966 20 210

(102a) A.B.P. Lever, Inorg.Chem., 1965 4 1042
R.H. Nuttall and D.W. Taylor, Chem.Comm., 1968 1417
F.A. Cotton, D.M.L. Goodgame and R.H. Soderberg, Inorg.Chem., 1963 2 1162
J.T. Donoghue and R.S. Drago, Inorg.Chem., 1963 2 572

(103) E. Grison, K. Eriks and J.L. de Vries, Acta Cryst., 1950 3 290
R.M. Curtis and R.A. Pasternak, Acta Cryst., 1955 8 675
A.J. Serewicz, B.K. Robertson and E.A. Meyers, J.Phys.Chem., 1965 69 1915
P. Cherin, W.C. Hamilton and B. Post, Acta Cryst., 1967 23 455

(104) C.A. Coulson, V. Henri Memorial Volume, Desoer, Liege, 1948, p15

(105) M.J.S. Dewar and H.N. Schmeising, Tetrahedron, 1959 5 166

(106) C.D. Garner, J. Hilton and S.C. Wallwork, Acta Cryst., 1969 A25 S104

(107) R.S. Mulliken, Tetrahedron, 1959 6 68
Reference (36) p311

(108) L. Pauling, 'The Nature of the Chemical Bond', 3rd ed., Cornell University Press, Ithaca, N.Y., 1960, p246

(109) C.D. Garner and S.C. Wallwork, J.Chem.Soc(A)., 1966 1496

(110) J.C. Taylor, M.H. Mueller and R.L. Hitterman, Acta Cryst., 1966 20 842
D. Britton and J.D. Dunitz, Acta Cryst., 1965 19 815

(111) C.D. Garner and F.E. Mobbs, J.Chem.Soc(A)., 1970 1711

(112) C.C. Addison, N. Logan, S.C. Wallwork and C.D. Garner, Quart.Rev., 1972 26 303

(113) J. Drummond and J.S. Wood, Abstract A.34, Chem. Soc. Meeting, Keele, 1968

(114) C.C. Addison, C.D. Garner, W.B. Simpson, D. Sutton and S.C. Wallwork, Proc.Chem.Soc., 1965 598
C.C. Addison and W.B. Simpson, J.Chem.Soc., 1965 598

(115) J.D. Dunitz, Acta Cryst., 1957 10 307

(116) M.A. Porai-Koshits, L.O.Atovmyan, G.N. Tischenko, Zh.Strukt.Khim., 1960 1 337

(117) M. Rosenthal and R.S. Drago, Inorg.Chem., 1965 8 840

(118) D.W. Herlocker and M.R. Rosenthal, Inorgan.Chim. Acta, 1970 4 501

(119) N.S. Gill, R.H. Nuttall, D.E. Scaife and D.W.A. Sharp, J.Inorg.Nucl.Chem., 1961 18 79

(120) C. Postmus, J.R. Ferraro, W. Wozniak, Inorg.Chem., 1967 6 2030

(121) J.R. Allen, D.H. Brown, R.H. Nuttall and D.W.A. Sharp, J.Inorg.Nucl.Chem., 1965 27 1305

(122) R.J.H. Clark and C.S. Williams, Inorg.Chem., 1965 3 350

(123) M. Goldstein, E.F. Mooney, A. Anderson and H.A. Gebbie, Spectrochim.Acta, 1965 21 105

(124) H.C. Volger and W. Brackman, Rec.Trav.Chim., 1965 84 1203

(125) H.C. Volger and W. Brackman, Rec.Trav.Chim., 1965 84 1233

(126) R.V. Biagetti, W.G. Bottjer and H.M. Haendler, Inorg.Chem., 1966 5 379

(127) P. Pfeiffer and V. Pimmer, Z.Anorg.Chem., 1906 48 98

(128) M. Ragno and L. Valada, Gazz.Chim.Ital., 1935 65 686

(129) H. Grossman, Ber.Deut.Chem.Ges., 1904 37 1253

(130) C.W. Frank and L.B. Rogers, Inorg.Chem., 1966 5 615

(131) N.G. Mitra and P.C. Sinha, J.Ind.Chem.Soc., 1950 27 29

(132) N. Logan and W. Simpson, Spectrochim.Acta, 1965 21 1253

(133) L.I. Katzin, J.R. Ferraro and E. Gebert, J.Amer. Chem.Soc., 1950 72 5471

(134) E.W. Abel and G. Wilkinson, J.Chem.Soc., 1959 1501

(135) C.H. Kline and J. Turkevich, J.Chem.Phys., 1944 12 300

(136) L. Corssin, B.J. Fox and R.C. Lord, J.Chem.Phys., 1953 21 1170

(137) J.K. Wilmshurst and H.J. Bernstein, Cand.J.Chem., 1957 35 1185

(138) L. Bicelli, Nuovo Cim., 1958 9 184

(139) G. Zerbi, J. Overend and B. Crawford, J.Chem.Phys., 1963 38 122

(140) L.C. Lewis, Diss.Abs., 1967 28 1841-B

(141) D.W. Taylor, M.Sc. Thesis, University of Strathclyde, 1969

(142) Y. Komiyana and E.C. Lingafelta, Acta Cryst., 1964 17 1145

(143) M.A. Porai-Koshits, Zh.Strukt.Khim., 1963 4 584

(144) D.S. Brown, J.D. Lee, B.G.A. Melson, B.J.Procter and A.A.G. Tomlinson, Chem.Comm., 1967 369
D.S. Brown, J.D. Lee and B.G.A. Melson, Acta Cryst., 1968 B24 730

(145) A.F. Cameron, R.H. Nuttall and D.W. Taylor, J.Chem. Soc(A)., 1971 3103

(146) R.L. Carlin and M.J. Baker, J.Chem.Soc., 1964 5008

(147) R.H. Nuttall and D.W. Taylor, Chem.Comm., 1968 1417

(148) W. Harrison and J. Trotter, J.Chem.Soc.(Dalton), 1972 956

(149) D.A. Langs and C.R. Hare, Chem.Comm., 1967 890

(150) W.H. Zachariasen and M.A. Plettinger, Acta Cryst., 1959 12 526

(151) D.M.L. Goodgame, M.A. Hitchman, D.F. Marsham, P. Phavantha and D. Rogers, Chem.Comm., 1969 1383

(152) Chem.Soc.Special Publ., No.11, 1959; No.18, 1965

(153) D. Hall and I. Robertson, private communication

(154) D.W. Smith, J.Chem.Soc(A)., 1970 176

(155) R.J. Gillespie in 'Advances in the Chemistry of Coordination Compounds', ed. S. Kirschner, MacMillan, London, 1967

(156) R. Stomberg, Arkiv Kemi, 1964 22 29

(157) W. Zachariasen, Acta Cryst., 1954 7 783
R. Stromberg, Arkiv Kemi, 1964 23 401, Nature, 1964 205 71

(158) R. Stromberg, Arkiv Kemi, 1965 24 111

(159) R. Stromberg, Nature, 1965 207 76

(160) R. Stromberg, Arkiv Kemi, 1965 25 47

(161) B.J. Hathaway and D.E. Billing, Coordin.Chem.Rev., 1970 5 143

(162) D.S. Brown, J.D. Lee, B.G.A. Melson, B.J. Procter and A.A.G. Tomlinson, Chem.Comm., 1967 369

(163) D.A. Langs and C.R. Hare, Chem.Comm., 1967 890

(164) C.D. Garner, P. Lambert, F.E. Mobbs and J.K. Porter, J.Chem.Soc.(Dalton) 1972 320

(165) R. Osterberg, B. Bjoberg, and R. Soderquist, Chem. Comm., 1970 1410

(166) R.J. Dudley, B.J. Hathaway and P.G. Hodgson, J.Chem. Soc(A)., 1971 3355

(167) D.E. Billing, B.J. Hathaway and P. Nicholls, J.Chem. Soc(A)., 1970 1877

(168) D.E. Billing, B.J. Hathaway and P. Nicholls, J.Chem.Soc(A)., 1969 316

(169) Chem.Soc.Special Publ., No.11, 1959; No.18, 1965 F. Durant, P. Piret and M. van Meerssche, Acta Cryst., 1967 22 52; 1966 75 806

(170) T.J. Ouellette and H.M. Haendler, Inorg.Chem., 1969 8 1777

(171) Chem.Soc.Special Publ., No.11, 1959; No.18, 1965 Also, References (80), (81), (169), (172)

(172) I. Agrell, Acta Chem.Scand., 1970 24 1247

(173) A.B.P. Lever, Inorg.Chem., 1965 4 1042

(174) F.A. Cotton, D.M.L. Goodgame and R.H. Soderberg, Inorg.Chem., 1963 2 1162

(175) R.J.H. Clark and C.S. Williams, Inorg.Chem., 1965 3 350

(176) R.V. Biagetti and H.M. Haendler, Inorg.Chem., 1966 5 383

(177) L.I. Katzin, J.R. Ferraro and E. Gebert, J.Amer. Chem.Soc., 1950 72 5471

(178) M.R. Rosenthal and R.S. Drago, Inorg.Chem., 1965 4 840

(179) D.W. Herlocker and M.R. Rosenthal, Inorgan.Chim. Acta, 1970 4 501

(180) C.W. Frank and L.B. Rogers, Inorg.Chem., 1966 5 615

(181) Chem.Soc.Special Publ., No.11, 1959; No.18, 1965
Also, References (72), (87), (97), (99)

(182) C.C. Addison and D. Sutton, J.Chem.Soc(A)., 1966 1524

(183) D.K. Straub, R.S. Drago and J.T. Donoghue, Inorg. Chem., 1962 1 848

(184) Chem.Soc.Special Publ., No.11, 1959; No.18, 1965
Also, References (115), (116), (190), (192), (193)

(185) L.E. Orgel, 'An Introduction to Ligand Field Theory', Methuen, London, 1966

(186) B.J. Hathaway and D.E. Billing, Coordin.Chem.Rev., 1970 5 143

(187) H.L. Schläfer and G. Gliemann, 'Basic Principles of Ligand Field Theory', Wiley-Interscience, New York, 1969, p172

(189) F.A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry', Wiley-Interscience, 1962, p479

(190) C.H. MacGillavry and J.M. Bivoet, Z.Krist., 1936 94 249

(191) As Reference (190)

(192) Yu A. Sokolova, L.O. Atovmyan and M.A. Porai-Koshits, Zh.Strukt.Khim., 1966 7 855

(193) C.H. MacGillavry and J.M. Bivoet, Z.Krist., 1936 94 231

(194) C.H. MacGillavry and J.M. Bivoet, Z.Krist., 1936 94 231

(195) R. Zannetti, Gazz.Chim.Ital., 1960 90 1428

(196) I. Agrell, Acta Chem.Scand., 1970 24 3575

(197) Chem.Soc.Special Publ., No.11, 1959; No.18, 1965
Also, References (193-6)
N.V. Podberezskaya, V.V. Bakakin, S.V. Borisov, Zh.Strukt.Khim., 1969 10 847
L. Cavalca, M. Nardelli and L. Goghi, Nuovo Cimento, 1957 6 278

(198) H. Irving and R.J.P. Williams, J.Chem.Soc., 1953 3192

(199) C. Calvo and J.S. Stephens, Cand.J.Chem., 1968 46 903

(200) C. Calvo and P.K.L. Au, Cand.J.Chem., 1969 47 3409

(201) A.B.P. Lever, Inorg.Chem., 1965 4 1042

(202) S.S. Kobalkina, Dolk.Akad.Nauk.S.S.S.R., 1957 110 1013
J.D. Dunitz, Acta Cryst., 1957 10 307

(203) V.F. Duckworth and N.C. Stephenson, Acta Cryst., 1969 B25 1795

(204) G. Davey and F.S. Stephens, J.Chem.Soc(A)., 1971 1917

(206) B.J. Hathaway, private communication

(207) S.F.A. Kettle and A.J.P. Pioli, J.Chem.Soc(A)., 1968 1243

(208) G. Davey and F.S. Stephens, J.Chem.Soc(A)., 1971 2577

(209) Chem.Soc.Special Publ., No.11, 1959; No. 18, 1965 Also, References (169), (203), (204), (208)

(210) W. Harrison and J. Trotter, J.Chem.Soc.(Dalton), 1972 956 and references contained therein

(211) T.N. Tarkhova and A.V. Ablov, Krist., 1968 13 611

(212) 'International Tables for X-Ray Crystallography', Vol.III, Kynoch Press, Birmingham, 1962